Institut für Siedlungswasserwirtschaft

84

Conference Proceedings

4th International Symposium "Re-Water Braunschweig"

Braunschweig, 06./07.11.2013

Veröffentlichungen des Institutes für Siedlungswasserwirtschaft
der Technischen Universität Braunschweig

Technische Universität Braunschweig

Heft 84 **Braunschweig 2013**

Institut für Siedlungswasserwirtschaft

84

Conference Proceedings

4th International Symposium "Re-Water Braunschweig"

Quality, Reuse, Global Aspects

Veröffentlichungen des Institutes für Siedlungswasserwirtschaft
der Technischen Universität Braunschweig

ISSN 0934-9731
DOI 10.24355/dbbs.084-202103230745-0

Herausgeber:

Gesellschaft zur Förderung des Institutes
für Siedlungswasserwirtschaft an der
Technischen Universität Braunschweig e. V.

Braunschweig 2013

Technische Universität Braunschweig

Preface

Quality, Reuse, Global Aspects

The main themes of the 4th International Symposium „Re-Water Braunschweig" are "Quality, Reuse, Global Aspects". These aspects are closely linked to each other – globally, the reuse of treated wastewater is a promising strategy to cope with water shortage and to protect resources. Within this context, "hygiene" always plays an important role, especially with regard to the reuse of water in agriculture. "Global aspects" are also addressed in various presentations focusing on (possible) future developments and on the transition processes within the field of sanitary and environmental engineering.

Corresponding to the title of the symposium, it also addresses the newest developments within the field of nutrient recycling on a regular basis. This year, special attention is paid on the link between nutrient recovery and nutrient reuse in agriculture and industry.

The symposium is organised by the "Stadtentwässerung Braunschweig GmbH". Cooperation partners are the Institute of Sanitary and Environmental Engineering of the TU Braunschweig, the Berlin Centre of Competence for Water and the "Abwasserverband Braunschweig". Further information and a detailed timetable under www.re-water.de.

Table of content

Greywater (re)use options in a German urban context – necessities, challenges, barriers

Jörg Londong, Susanne Scharf, Stephanie Klein

Bauhaus institute for infrastructure solutions, Bauhaus-Universität Weimar

Abstract

Based on a sustainability management of our water resources and closed loop systems for wastewater management the development of new sanitary systems is currently under discussion in Germany. Dynamics like climate or demographic changes require new flexible and reliable wastewater systems. Therefore greywater (re)use in German urban context possess' a high potential as a part of new sanitation systems.

Greywater (re)use options are various in a German urban context but up to today they remain options and not solutions. In order to promote greywater (re)use in Germany it is mandatory to deal with its necessities, challenges and barriers.

1. Introduction

In Germany the development from dispose to utilise used resources has mainly been considered in waste management and is now laid down in a new waste management act. In spite of this development and the existing technologies the idea of a sustainable management of water resources including treatment and reuse has not been fixed in the German legislation and German society yet. Nevertheless a working group in Germany has collected the knowledge concerning new and alternative sanitation systems (NASS) [DWA, 2008] and proposes the integration of NASS in all design processes in sanitation planning [DWA, 2013].

Focussing on water, energy and nutrient reuse it is advantageous to separate sewage flows at the source. An example of such a NASS with flow separation of greywater is shown in figure 1.

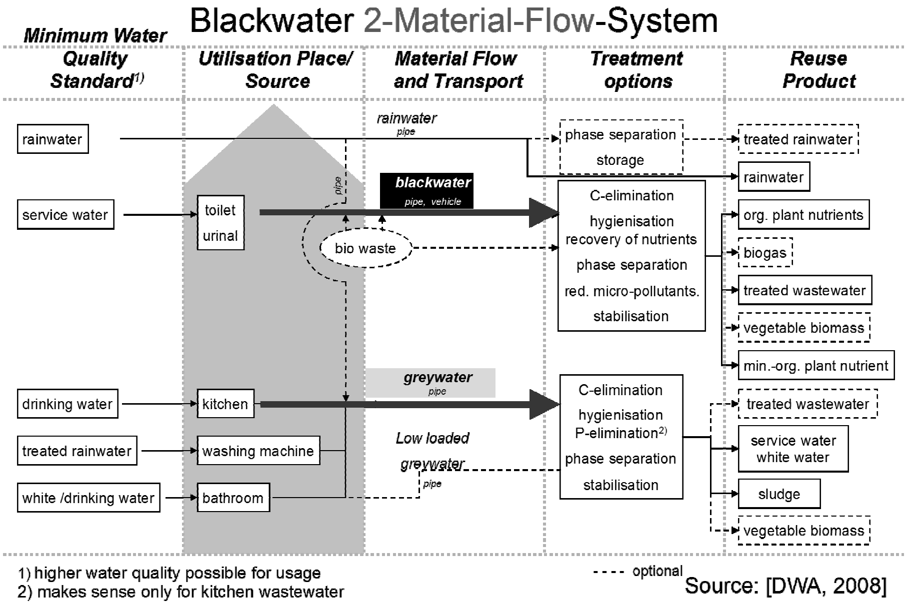


Figure 1: Blackwater 2-Material-Flow-System

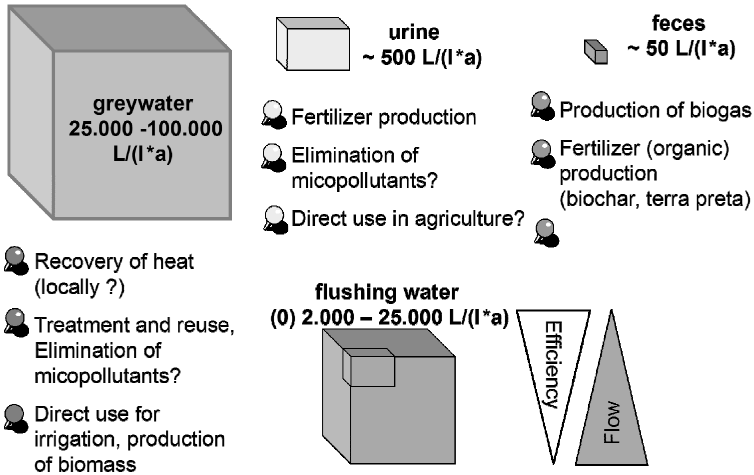


Figure 2: Potentials and challenges of source separation in sanitation

Within NASS greywater consists of the potential for water (re)use and good availability. The advantages of greywater are well discussed and based on the high volume flow and the low pollution. Recently this potential is used in arid areas of the world. But although Germany does not suffer from water scarcity there are also greywater (re)use options which could be implemented in German water management strategies – especially for urban areas. And it has to be questioned why up to now most of them remain options and not solutions.

2. Greywater (re)use options in a German urban context

If greywater would be used consequently, there must be an option for the remaining blackwater and vice versa. Using the existing sewerage for blackwater only, is not an option due to operational reasons. Separating blackwater in order to produce energy and fertilizer and to discharge greywater in the existing sewerage would mean that the sewerage has to be operated further on and reinvestments to keep it water tide would be a consequence. Therefore greywater and blackwater (re)use options have to be handled in a system context of all wastewater flows.

Greywater use could serve as substitution for potable water but different than in arid areas not for drinking purposes. Greywater as substitution for potable water means use as service water on a household level or in order to cover industrial or public demands.

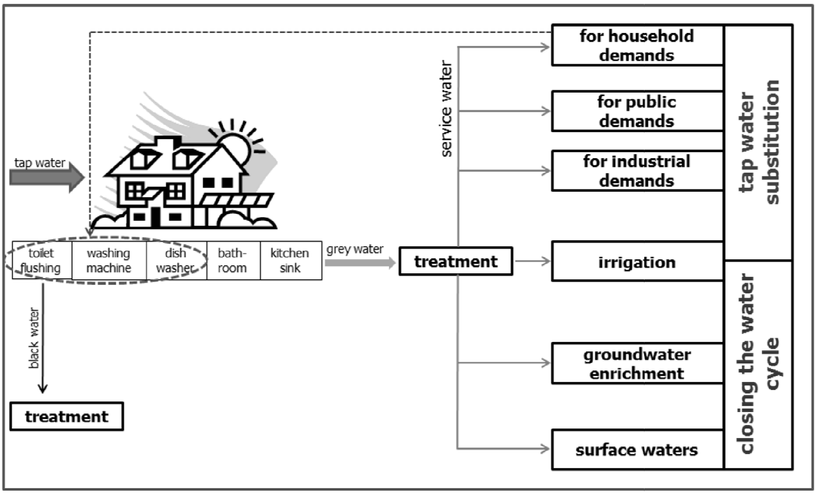


Figure 3: Greywater (re)use options in a German context

All three sectors consist of different opportunities to use treated greywater. The industrial demand depends recently on the industrial or business sector. In the public sector greywater could be used for irrigation, street cleaning, car washing or for fire fighting purposes. Water reuse on a household level could be realized as service water in case of toilet flushing, water for washing machines, dish washers or irrigation as well. The greywater (re)use for drinking or personal care demands is not conceivable in Germany.

Alternatively to service water greywater could contribute to groundwater enrichment (by infiltration) or recharging of surface waters (i.e. by discharge in receiving waters). An overview of greywater (re)use options is shown in the following figure. Apart from the water (re)use of greywater it also could be used for heat recovery.

3. Necessities, challenges, barriers

The idea of source separation and making use of greywater is comparatively new in the German sanitation system [Londong, 2013]. And as usual new technologies have to manage different challenges and fight against resistances until their final admission and final acceptance. But in contrast to many other new ideas greywater use has to manage challenges on several fields (as shown in figure 4).

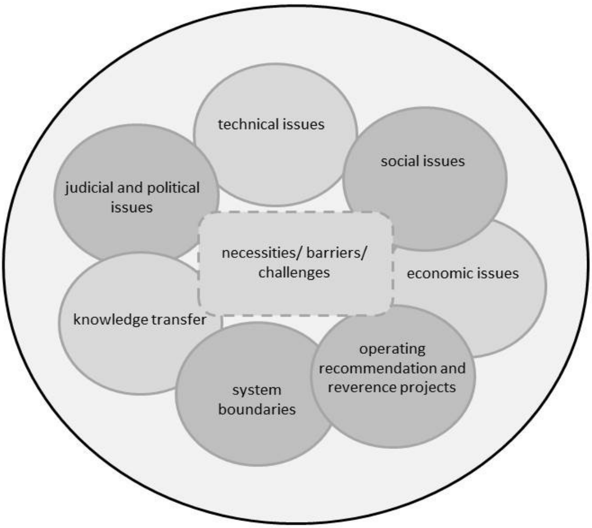


Figure 4: Interlinking sectors for the implementation of greywater (re)use

3.1 Motivation issues

As Germany does not suffer from water scarcity the assumed most important reason for greywater reuse is not appropriate. Hence it follows there is a lack of motivation to think about water saving and reuse opportunities. This lack of motivation is strengthened because - in comparison to the waste management sector - there is no direct ecological necessity for a change in the sanitation system yet. Consequently society and authorities do not promote any changes.

But Germany has the highest rates for water and wastewater services in Europe [Bieker and Birte, 2010]. Maybe new sanitation systems could participate on the efforts to lower these rates. Especially against the background of the demographic changes new sanitation systems could be an alternative to the existing expensive and inflexible wastewater service system. [Londong et al., 2011]

The current condition of the sewer system in Germany could be a starting point for the change of the sanitation system – from a system based on dilution to a system of (re)use based on separation of different wastewater streams. In an intermediate term 20% of private sewer systems and 40% of public sewer systems are classified as in need of rehabilitation [Bieker and Birte, 2010].

Additionally the influence of the demographic and climate change should not be underestimated. That means on the one hand shrinking semi-urban cities with declining numbers of inhabitants, oversized supply and disposal systems, under-utilization of networks and systems, strong operational problems in water supply and sanitation. On the other hand that means ever-growing cities, which are especially characterized by rapidly increasing numbers of inhabitants, compression of settlement areas and the expansion of suburban areas [Hillenbrand, 2012].

It is obvious that both developments will cause problems regarding the sanitation system. These problems will be different but have to be solved. And even if the existing sanitation system is able to solve these problems it would be hard to afford. But one possible solution could be the (partly) implementation of new sanitation systems.

3.2 Regulation issues

All greywater options require greywater treatment according to the intended way of water reuse. But up to today there are no mandatory regulations for each reuse option in general. Only irrigation (in public areas!) and its demands regarding water quality are fixed in DIN 19650.

Groundwater enrichment as well as discharge in surface waters requires a water quality consent, which has to be applied, proven and authorised on an individual basis. Service water for use in public areas is defined in DIN 4046. Regulations for the greywater quality, which could be used as service water, do not exist. So the EU Bath Water Directive is used as a substitute to define the quality of toilet flushing water for example. There have not been any regulations with regard to service water for washing machines or dishwashers yet. The legal framework for greywater reuse in private households also does not exist.

Apart from these regulations it has to be discussed if the implementation of greywater treatment plants or of any other wastewater treatment plant in general fulfil the requirements of the German compulsory use.

Without these necessary law and regulation frame work no planer will be willing to implement greywater (re)use in any project.

3.3 Economic issues

The implementation of different subsystems in the sanitation system will raise questions about economy: How to design an equitable funding system and how to allocate costs to the consumers? Different systems require different costs, which have to be covered by the customers. But is it possible to have different fees and fee systems for the same community service in one community?

Apart from this greywater treatment and use can be expensive depending on the different treatment requirements. Especially the increasing number of treatment plants and increasing requirements of performance reliability could be cost-intensive [Ziedorn, Meinziger and Peters, 2007]. So it is necessary to calculate in every single case which system is cost efficient and should be implemented.

Finally the building costs for wastewater treatment plants are not insignificant and often realized by public funding. But public funding is up to today based on the requirement of conventional wastewater concepts [Hillenbrand, 2012].

3.4 Social issues

Most people are not interested in thinking or talking about their sanitation. And because of the centralised sanitation system in most parts of Germany thinking about sanitation is obsolete. But the (re)use of greywater requires to think about sanitation and to make several decisions. And without social acceptance there will be no progress and no paradigm shift.

Additionally the existing centralized supply and sanitation system guarantees supply and disposal security on a very high level. Greywater usage systems have to guarantee the same comfort as well. Otherwise social acceptance problems will occur inevitably.

3.5 Technological issues

The technological aspects of greywater collection, treatment and use are well discussed. A few treatment systems are available on the market. But there are still a number of research and development questions left.

Although a mass of publications deal with greywater characteristics, reliable data (like specific loads in g/(person.d)) for design are lacking.

It is still questionable whether the entire greywater can be used as service water or only a particular part. Therefore it is also necessary to examine if one greywater source (bathroom, kitchen, washing machine) is less or more applicable for reuse than other ones.

Micro-pollutants in greywater are an upcoming Problem. A BUND study [BUND, 2013] outlines the presence substances with hormonal effects in about one third of personal care products. After use these substances may enter greywater. Research on endocrine substances and other micro-pollutants in greywater and their effect on treatment an (re)use options have to be examined. In this context the effects of different greywater ingredients on blackwater treatment – in case of greywater use for toilet flushing - should be considered. The existence of extraneous materials for anaerobic processes would be a barrier for greywater (re)use for toilet flushing and consecutive blackwater treatment. The answers to these questions may lead to different treatment and separation demands.

The storage of treated greywater is up to today an unsolved problem. The high temperature range increases the risk of re-contamination [Bieker and Birte, 2010; Kaufmann Alves et al., 2008].

Heat recovery could be a solution for the re-contamination risk. But heat recovery leads to further questions relating to a capable technology. First of all it is to decide where to implement heat recovery in the treatment process – previous to the treatment process or afterwards. Both possibilities imply different challenges and demands. On the one hand heat recovery implementation previous to preliminary treatment will lead to problems relating to suspended solids or even to fouling processes. On the other hand heat recovery implementation after treatment could go along with heat loss and a reduction of treatment options. This is one of the research questions, which will be dealt with in the TWIST++ project [www.twistpluplus.de].

In comparison to new building projects it is a lot more complicated to implement greywater treatment and use in already existing infrastructures [Kaufmann Alves et al., 2008]. Applicable solutions for greywater separation in existing houses are not available yet.

All technologies have to be compatible to the challenges by city development. It is expected that cities in metropolitan areas will grow fast and continuously. Greywater treatment technologies should therefore be flexible and reliable as well [Bieker and Birte, 2010].

Another technological aspect could be the use of treated greywater for fire fighting purposes [Hiessl, 2008]. But this requires the separation of fresh water supply and fire fighter water supply first.

3.6 Issues of knowledge transfer

New sanitation concepts are well discussed in research and development projects. But they can only be implemented if all relevant stakeholders in planning processes, decision making processes, administration, building processes, operation and maintenance are familiar with them.

So it is mandatory that new sanitation concepts have to be part of the academic education, practical training and advanced training.

3.7 Issues of system boundaries

The current sanitation system in Germany is inflexible and cost-intensive. New influences are not only necessary but also inevitable [Ziedorn, Meinziger and Peters, 2007]. But it is obvious that a nation-wide change will not take place. So a combined system will be the solution anyway. But how can such a combined system be designed in order to have less conflicts and a safe operation as well? And it is also obvious that there will not be one significant combined system only but very different ones depending on different forms of residential areas and specific local demands. Paying attention to the transition phases is an important aspect of system changes.

It is necessary to define system boundaries in each several case. Referring to the implementation of greywater use it will be inevitable to consider blackwater and rainwater as well. The implementation of water reuse requires the separation of rainwater in any case [Bieker and Birte, 2010]. It is not reasonable to separate and treat wastewater flows in a decentralized way and to discharge low contaminated rainwater into a centralised wastewater treatment plant.

It will also not be possible to except greywater from the existing sanitation system. This would cause problems with the water-borne sewage system. And even without the separation of greywater there are already existing problems with die water-borne sewage system because of lower water consumption and along going lower waste water volume flow [Bieker and Birte, 2010; Londong et al. 2011]. So temporarily flushing of the sewer with tap water is the consequence in order to compensate the upcoming problems. To implement greywater use in such a system would increase the problem and lead the idea of water saving ad absurdum.

Greywater use on a household level will reduce the demand of tap water especially if greywater is used for toilet flushing. In spite of this the amount of produced greywater for use is possibly higher than the consumption in the household. This requires a system for the disposal of the excess water. Otherwise another use option for greywater has to be found within the reach of the greywater source.

Additionally it is to consider that also a disposal system is needed if several wastewater flows are not separated and treated completely in an entire area [Kaufmann Alves et al., 2008].

Up to now there are a few pilot projects including greywater treatment and use but there have not been many results for projects considering greywater use in entire areas. The pilot projects determine interesting water saving potentials especially for single commercial locations with high drinking water demand and high greywater flow as a consequence (i.e. hotels, camping grounds, sport complexes, residential homes ...). But referring to the entire sanitation system in an area it is necessary to discuss if it is reasonable to separate these locations from the public sanitation system and which could be the consequences.

4. Conclusions and outlook

The potential of greywater (re)use is immense – not only in areas of the world which suffer from water scarcity. There are a lot of reasonable aspects for greywater (re)use in Germany both in rural and urban areas, too. Effects like demographic change, climate change or the sewer system’s condition in Germany increase the possibilities and necessities for a paradigm shift in the sanitation sector including greywater (re)use. But a paradigm shift is always connected with a multitude of necessities, challenges and barriers, which could be subsumed under different complexes. Technical innovations are linked to economic issues and knowledge transfer is always required. In consideration of the wastewater topic it is not remarkable that there are social or acceptance questions. As this paper is dealing with the German context, it is also not remarkable that legal regulations and the praxis of approval procedures are severe obstacles. It is remarkable that there are so many system boundaries issues. This is a consequence of the complexity of the German sanitation system and the necessity of a change within the system without the possibility to chance the whole system. That leads to a hardly changeable framework.

Actually several research and development projects try to generate experiences in different issues in relation to greywater implementation, in particular respectively implementation of new sanitation systems in general in Germany. Some examples - our institute is engaged in - are marked below:

4.1 KREIS – Linking sustainable energy generation to urban waste water generation

KREIS is researching new infrastructure concepts to serve urban residential districts. It focuses on wastewater disposal and energy supply as complementary partners with similar topics. Research topics are on the one hand technologies and concepts for energy supply, wastewater treatment and reuse of residual materials. On the other hand the ecological, economic and social effects of these new technologies and concepts are investigated.

The combination of utilizing new sanitary concepts and generating energy out of renewable resources represents a visionary solution. Nevertheless it will be implemented, evaluated and further developed in a realistic urban project called “Jenfelder Au” in Hamburg, Germany. Here the HAMBURG WATER CYCLE ® as an innovative urban wastewater system will be supplemented by sustainable energy generation to meet the demand for energy, especially for heating. [www.kreis-jenfeld.de]

4.2 TWIST++ - Intelligent transition approaches for water infrastructure systems

The creation of a flexible system with respective to the amendment of ecological quality generates the interlinking of water supply and wastewater treatment.

The project emphasizes a conceptual and planning approach and is complemented with the development and adaption of specific individual technologies through the integration of transmission and management strategies. The feasibility will be tested and implemented on the basis of three different model regions: a shrinking city close to the Ruhr-district, a brownfield in the middle of an urban area and one shrinking and one growing village in Thuringia rural environment.

The three different model areas have representative boundary conditions for many places in Germany. Not only new technologies can also be established to identify drivers and barriers as well as the necessary institutional framework for the implementation of major planning and evaluation tools are required.

An inherent part of TWIST++ is to define a complete system for a decentralized wastewater treatment. The concepts are verified using concrete design alternatives.

This includes the identification and testing of appropriate technologies for greywater treatment. [www.twistplusplus.de]

4.3 EVaSENS – Tube-in-tube reconstruction in combination with vacuum technology

Aim of the research and development project to examine, whether it is possible to equip existing house installations with a separate blackwater pipe by introducing 2 differently sized liners.

If the project is successful, the new method of lining two pipes into the old existing installation would allow to implement a vacuum blackwater and a gravity flow greywater system in existing houses. [http://www.uni-weimar.de/Bauing/siwawi/forschung/_projekte/aktuelle/EVaSENS-eng.htm]

References

Bieker, Susanne & Frommer, Birte (2010): Potenziale flexibler integrierter semi-zentraler Infrastruktursysteme in der Siedlungswasserwirtschaft, Raumforschung Raumordnung 68, S. 311-326.

BUND (2013) Der Kosmetik-Check, Hormone in Kosmetika, http://www.bund.net/fileadmin/bundnet/publikationen/chemie/130723_bund_chemie_kosmetik_check_studie.pdf

DWA (2008) DWA-Themenband „Neuartige Sanitärsysteme“. DWA, Hennef, ISBN 978-3-941089-37-2

DWA (2013) DWA A 272: Grundsätze für die Planung und Implementierung Neuartiger Sanitärsysteme, Gelbdruck

Hillenbrand, Thomas (2012): DWA-A 272 – neues DWA-Arbeitsblatt zur Umsetzung neuartiger Sanitärsysteme, Beitrag im Rahmen der NASS-Tage 6.-7. November 2012: Neue Wasserinfrastrukturkonzepte in der Stadtplanung – Inklusive der Ergebnisse des Forschungsvorhabens SanitärRecycling Eschborn, Eschborn.

Hiessl, Harald (2008): Zukünftiger Umgang mit Wasser in Gebäuden – Anpassung an geänderte Randbedingungen, in: Fachvereinigung Betriebs- und Regenwassernutzung e.V. (Hrsg.): Innovative Wasserkonzepte in Gewerbe und Industrie sowie im Gebäudebestand, Schriftenreihe fbr 11, Darmstadt, S. 15 – 36.

Kaufmann Alves, Inka; Knerr, Henning; Schmitt, Theo G.; Steinmetz, Heidrun (2008): Auswirkungen der Integration neuartiger Abwasserentsorgungskonzepte in bestehende Infrastruktursysteme, Korrespondenz Abwasser, Abfall (55), S. 1074-1084.

Londong, Jörg (2013), Practical experience with source separation in Germany Chapter 29 in: Source Separation and Decentralization for Wastewater Management, IWA Publishing, London, UK, ISBN 9781843393481, pp. 423-430

Londong, Jörg, Hillenbrand, Thomas und Niederste-Hollenberg, Jutta (2011). Der demografische Wandel: Anlass und Chance für Innovationen in der Wasserwirtschaft,   KA Abwasser Abfall 58 (2011), H. 02, S. 152-158

Ziedorn, Volker; Meinziger, Franziska; Peters, Irene (2007): Städtische Siedlungsstrukturen und dezentrale Abwassersysteme- Möglichkeiten zum Einsatz innovativer Abwasserreinigungsanlagen im Bestand, Städtische Siedlungsstrukturen und dezentrale Abwassersysteme, Raumplanung 136, S. 16 -20

Authors

Univ.-Prof. Dr.-Ing. Jörg Londong

Susanne Scharf M.Sc.

Dipl.-Ing. Stephanie Klein

Bauhaus-Institute for infrastructure solution

Professur Siedlungswasserwirtschaft

Fakultät Bauingenieurwesen, Bauhaus-Universität Weimar

Coudraystr. 7

99423 Weimar

e-Mail: joerg.londong@uni-weimar.de

Appropriate Technologies for the Production of Hygienic Safe Sewage Sludge and Fertilizers

Björn Vinnerås, Annika Nordin

Swedish University of Agricultural Sciences, Uppsala

Abstract

In a sustainable society the plant nutrients from the wastewater needs to be recycled back into food production. With the excreta originated nutrients follows the risk for transmitting disease causing microorganisms to domestic animals. The disease transmission needs to be stopped before the nutrients are recycled. In this paper different hygiene treatment requirement for heat, biological and chemical treatment are described and compared for countries in Western Europe and USA.

Keywords: ammonia, heat, lime, hygiene, sanitisation

1. Introduction

In society of today the flow of plant nutrients are mainly linear from the field with the produce to the water recipient via the food that is consumed by humans. It is only very little of the plant nutrient that is recycled back to agricultural production. When looking at the global sanitation, half is water based, where only half of that is treated by any means at all; the remaining is released more or less directly into the water courses untreated. The remaining part of the population does half have dry sanitation and the remaining does not have access to any proper sanitation at all (http://www.wssinfo.org/).

By recycling the nutrients back into the agricultural production the need for antropogenic nutrients decreases and thereby decrease the consumption of virgin resources. The potential of plant nutrients in the toilet fraction correspond to 21, 32 and 26% of N, P and K, respectively for Germany and 25, 50 and 56% of N, P and K, respectively for Sweden (Clemens et al., 2012).

The interest for new sanitation systems is growing in Europe with a focus on urine diversion and blackwater systems that can recycle large amounts of the nutrients in wastewater. The main nutrient fraction available today for recycling is sewage sludge, which is a phosphorus rich fertiliser. For the sewage sludge to be recycled the heavy metal content of the sludge has to be low enough to not contaminate the land. The heavy metal contamination can to a large extent be seen as an effect from industrial connection to the sewer system and when having heavy metals contamination of the sludge it cannot be processed into a usable fraction and have to be managed by upstream actions. Other contaminants such as organic substances and hygiene factors are possible to manage by treatment (Vinnerås et al., 2008b). The organic pollutants are an emerging factor as the use of chemicals in society is increasing. However, the main impact from these substances has been found in water fractions and not soil.

Hygienic quality is the crucial factor for the reuse of these substances in agriculture due to the risk of spreading diseases by applying organic waste and wastewater fractions as a fertiliser. When closing the loop of plant nutrients the loop of disease causing microorganisms (pathogens) will be closed as well. Therefore, the value chain for converting wastewater fraction into fertilisers has to take into account the possibility to break the risk of disease transmission.

The objective of this paper is given an overview about the legislation regarding reuse of human waste in correlation to the hygienic quality and proposed treatment methods for appropriate reuse in agriculture.

2. Why sanitise

Closing the loop of nutrients we risk of closing the loop of pathogens and when changing current system to a more recycling one, the risk for transmitting disease increases as one more route of transmission is introduced. The route of disease transmission needs to be broken in order to produce safe food. Each step of treatment increases the biosafety of the fertiliser product. Regarding the plant nutrients we find the opposite as each stage of treatment increase the risk of losing nutrients. In a recycling system these two factors of risk for disease transmission and plant nutrient management has to be weight against each other.

For the hygiene management a sanitisation level for what can be acceptable has to be set, i.e. how many person’s risk to be infected by a management principle. This decision combined with the estimated level of pathogens in a material and the infection dose of the specific organisms can be summarised into a required reduction level for a set of organisms. Most often indicator organisms are used for the full set of disease causing microorganisms that can be detected in the material (Table 1). What organisms and the acceptable level varies in different countries, an most often is the level set in correlation to other factors and their risk for disease transmission. The largest difference in acceptable level is the lowest acceptable level of *Salmonella* spp. where

Norway and Germany do not accept any salmonella in 50 g samples while Italy accept up to 10 000 cfu per gram material. This is probably correlated to the concentration of salmonella that is found in agriculture in the region.

Table 1: Pathogen limits in sewage and manure to be used in validation of sludge management processes

Organism	Detection level	Country
Enterobacteria	10^2 g^{-1} TS $<10^3$ g^{-1} TS	Luxemburg, Switzerland Austria
Thermo tolerant coliforms	$<10^3$ g^{-1} TS $<2.5\times10^3$ g^{-1} TS $<2\times10^6$ cfu/MPN g^{-1} TS Not be detected	USEPA Class A Norway USEPA Class B France
E.coli	$<5\times10^2$ g^{-1} TS $<10^3$ g^{-1} TS $<10^5$ g^{-1} TS 2 $\log_{10}$ reduction concentional) $<10^3$ g^{-1} TS 6 $\log_{10}$ reduction	EC sludge proposal Finland UK Conventional UK conventional, EC proposal UK enhanced UK enhanced; EC proposal adv treat
***Salmonella* spp**	Not detected in 1 g^{-1} TS Not detected in 25 g^{-1} ww Not detected in 50 g^{-1} ww <3 MPN 4 g^{-1} TS <8 MPN/10 g^{-1} TS $<10^3$ mpn g^{-1} TS (Italy) 5 $\log_{10}$ reduktion	Austria Finland EC proposal; Norway; Germany USEPA Class A France Italy S. Senftenberg W775; EU-ABP regulation
***Enterococcus* spp.**	< 100 g^{-1} 5 $\log_{10}$ reduction	Denmark EU-ABP regulation
Parasite ova (*=viable)	<3 10 g^{-1} TS <1 g^{-1} TS None 3 $\log_{10}$ reduction during chemical treatment	France USEPA Class A*; Austria, Switzerland Luxemburg; Norway* EU-ABP regulation
Virus	<1 4 g^{-1} TS <3 MPN 10 g^{-1} TS 3 $\log_{10}$ reduction	USEPA Class A France EU-ABP regulation (if virus are considered a risk

In most cases, the sanitisation level has to be validated in correlation to the performed process and some process parameters. Different countries have different parameters that regulate the level the actual validation. In some cases the se treatment alternatives, e.g. a specific temperature during a specific time period, is enough for the treatment. In other cases the authorising body require that the process is validate to deliver a certain level of reduction of a set of indicators and in some cases is a repeated revalidation required.

In some of the requirements in Table 1, a lower level of organism concentrations are set as the requirement. This level is based upon the concept that below this limit the risk of disease transmission is low enough, e.g. <100 cfu, g^{-1} TS. For other systems the requirement is that the treatment should deliver a certain reduction, e.g. 5log10 reduction. Both deliver the same safety level if the initial concentration of organisms is less than 7log10, g^{-1} TS. With the detection limit it is actually possible to dilute the sample to reach the lower limit, and the problem is also that with material of low dry matter content, e.g. human urine, the detection level is over 100 times higher than the acceptance limit making it impossible to prove that the limit is reached.

3. Organisms

The simplest microbial analysis is bacterial analysis and in all waste water products high initial levels of *Enterobacteriaceae* is found. Within this group you can find *Escherichia coli* as well as *Salmonella* spp. and they are included in the required hygienic standards of most recycling products. Thermo Tolerant Coliforms mainly consist of *E.coli* as well. The group is a good indicator for thermal inactivation treatment as the organisms within the group has high temperature resistance compared to many other indicators and pathogens at temperatures in the interval 50-60 °C (Vinneras et al., 2003b). For other treatments such as chemical treatment the group is considerably more sensitive compared to other organisms (Nordin et al., 2009; Vinnerås et al., 2008a).

Enterococcus spp. is also found at high initial levels in wastewater products and is therefore suitable as indicator of treatment efficiency. There are no pathogens found in the group so the inactivation does not reflect actual pathogen inactivation. However, there is a large potential for using *Enterococcus* spp. as a more conservative indicator for pathogenic organisms when linking the separate inactivation to a specific treatment.

Parasites are not as common as indicator of treatment performance, especially as they are considerably more complicated to cultivate and enumerate compared to bacteria. In North-western Europe the number of parasites to be found in waste water products are generally low (Sahlstrom et al., 2004). However, parasites are commonly used as performance indicators for chemical treatments as they are considerably more resistant than other organism groups. Within the Animal By Product regulation all chemical treatments has to be evaluated regarding its effect upon the survival of *Ascaris* spp. For heat treatment the inactivation of *Ascaris* spp. is generally faster at treatment temperatures at 50-60 °C compared to *Enterobacteriaceae* (Vinneras et al., 2003a). However, the Z-value of ascaris is lower which leads to that ascaris is more resistant at temperatures above 60°C compared to *Enterobacteriaceae*.

Virus can be divided into two categories, bacterial (phages) and animal viruses. Bacterial viruses that infect coli bacteria, coliphages, can always be expected in wastewater fractions while the content of animal/human viruses correlated to the infection rate in the persons connected to the system. Phages are considerably easier to cultivate compared to animal viruses and are therefore often used as indicators for animal viruses. The large variety of animal virus types gives a large distribution in sensitivity to a variety of treatments. There are only a few countries that regulate virus content in the wastewater products to be recycled and for ABP material such as manure is viruses only considered if it is looked upon as a risk (Table 1).

4. Treatment alternatives

Heat treatment is the most common and well evaluated treatment alterative for recycling of wastewater products. The time of the treatment is closely related to the temperature and the logarithm of the decimal reduction time is linear to the temperature for inactivation, the Z-value (given as degree Celsius to change the decimal reduction value one log10).

Pre-pasteurisation is the most common treatment alternative for sanitisation in combination to mesophile anaerobic treatment. By heating the material to a temperature above 50°C during a set time is it possible to inactivate appropriate number of microorganisms to decrease a risk for disease transmission. In Table 2 is the time and temperature requirement for pre-pasteurisation in several European countries and USA. When treating at high temperatures will some of the more complex organic substances found in the material become hydrolysed which result in a higher availability of the organic matter. At normal treatment temperatures, up to 70°C are the added gas production minimal for sewage sludge products, while some gain can be seen for more complex substrates such as food waste.

Table 2: Treatment alternatives included in regulations regarding production of safe fertilisers. Main regulation is related to sewage sludge, with the exception of animal manure marked by*

Treatment	Temp.	Time	Other requirement	Regulation/ Country	Clasification
Heat treatment	≥180°C	30 min		US EPA Part 503	Klass A
	≥80°C	-	a) combined with drying to <10% water content[a,b,c] b) > 10 min	US EPA Part 503[a] UK Code[a, b] EC proposal 2000[a, c]	Klass A Enhanced Advanced
		90 min	Combined with lime and drying	Norway	
	≥70 °C	1h		EC 1069/2009*	
		30 min		US EPA Part 503	Klass A
		30 min	Followd by mesophilic digestion 35°C MRT 12 days	UK Code EC proposal 2000	Enhanced Advanced
	≥65°C (70°C)	30 min			
	≥50°C	According to equation	$T(h) = 4{,}7 \times 10^{26} \times t^{-14{,}47}$	US EPA Part 503	US EPA Part 503
Storage		>6 months	*	UK 2009	Conventional
		>3 år	Dewatered sludge	Norway 2003	

Post-pasteurisation is another alternative treatment, the concept is the same as the pre-treatment, and there is no difference in requirement for time of treatment, but the treatment is performed after the biological treatment. The main risk with this kind of treatment is the risk for regrowth or contamination and growth of pathogenic bacteria in the material. The growth is due to the low number of bacteria in a heat treated substrate and the bacteria fastest to grow can colonise it. Due to the fast growth of intestinal bacteria they are often found soon after the treatment in high numbers. Additional stabilisation treatment is required, examples of this is post composting or ammonia treatment (below).

4.1 Biological heat treatment

When performing anaerobic digestion in the thermophilic temperature range can the high treatment temperature be used for sanitisation. Most important in a continuous treatment system is the minimal retention time, i.e. the shortest time between filling and emptying. In Norway when the minimal retention time at 55°C is set to be two hours (Table 2) is this treatment possible to use as hygiene treatment. While when having longer required time for treatment at these temperatures, e.g. 20h in the EC proposal for sludge management result in too long time between feeding to have a proper process design and stable process (Table 3a,b).

Table 3a: Biological heat treatment and required time of treatment at different temperatures in different countries

Treatment	Temp.	Time	Other requirement	Regulation/ Country	Clasification
Thermo-phile	≥55°C	4 h Eq1 63h	Aerob and anaerob treatment	UK Code USEPA	Enhanced Class A
Com-posting	≥60°C	4 h; HRT >5 dys	Followed by 10h at 55ºC & 20 h at 50°C	Germany	
		Eq1 13h		USEPA	Class A
	55°	22h		Germany	
		1h (1.5h)	Norway (pre treatment)		
	≥ 55°C	20 h		EC proposal 2000	Advanced
		90 min (120 min)	Norge; semi cont, draw and fill		
		12 h	min 4 h between each of 3 required mixing	UK Code	Enhanced
		3 days	With forced areation	US EPA Part 503	Class A
		4 h	Followed by 5 days above 40ºC;	UK Code[a] USEPA Part 503	Enhanced Class B
		1 week		WHO 2006	
		10 days	Liquid composting	US EPA Part 503	Class A
		20 dagar		EC proposal 2000	Advanced
	≥ 20°C	40 days	Anaerobic digestion	USEPA Part 503	Class B
	≥ 15°C	60 days	Anaerobic digestion	USEPA Part 503	Class B

In most cases the long time between fillings will result in that an additional hygiene treatment will be required. The other alternative is to perform the treatment at hyper thermophilic temperatures above 60°C where the time between fillings can be short in most cases (Table 2). In some cases further treatment at somewhat lower temperatures are required for the shortest retention times (Table 3a,b). The US, EU and UK treatment alternatives have two alternative treatment levels that is connected to intended use of the sludge. Where a higher hygienic requirement is set for sludge intended to be used in food production compared to other uses.

Table 3b: Biological heat treatment and required time of treatment at different temperatures in different countries

Treatment	Temp.	Time	Other requirement	Regulation/ Country	Clasification
Anaerobic digestion	≥ 53°C	20 h	Batchwise treatment	EC proposal 2000	Advanced
		Eq1 120h		USEPA	Class A
	35-55°C	15 days		USEPA EC proposal 2000	Class B conventional
	32-38°C	12 days	MRT followed by 2 weeks secondary treatment	UK	conventional
	≥ 20°C	60 days		USEPA	Class B

In liquid composting the aerobic treatment produce enough heat energy for heating the material. The function is that slurry with dry matter content below 10% is aerated and mixed for high aerob biological activity. In some cases, the treatment is used as an alternative for sewage sludge treatment for stabilisation and sanitisation. It can also be used as the sanitising and heating step prior or after anaerobic treatment. In Scandinavia has the method mainly been used for treatment of source separated toilet water, even called blackwater. In Sweden, three treatment systems have been constructed with this purpose. In all systems, the solids content has been too low to reach sanitising temperatures above 50°C during the required time interval. Therefore, most treatments require an addition of other organic matter to reach temperatures above 50°C, most often is animal manure that does not require sanitisation used. Liquid composting is an established technique, and mainly performed in small to medium scale, up to 1000 ton per year. It is a costly system to run as it has high energy demand for the aeration, especially if additional organic matter, that does not require sanitising treatment, is used.

One alternative treatment is to combine a temperature above 30°C with post treatment by ammonia, in an isolated reactor. By this combination the ammonia treatment can be performed at high temperature and therefore be performed during a short time period. After the ammonia treatment the heat is exchanged back into the incoming material (Nordin and Vinnerås, 2013). The function of the ammonia treatment is presented below.

4.2 Chemical treatment

Lime treatment can be performed in two different versions, either by using slaked lime where the treatment is based on elevated pH, or by addition of burned lime that result in elevation of both pH and temperature.

Slaked lime treatment returns an increase in pH and for removal of bacteria pathogens, e.g. *Salmonella* spp. there is enough to reach a pH of eleven and above (Nyberg et al., 2011), but for a general sanitisation pH above 12 is recommended during 3 months for safe sanitisation (Table 4), the German regulation specify pH 12.8 during three months for sanitisation.

The high pH affect the ammonia content of the material leading to high risk of air emissions of ammonia during treatment. Carbon dioxide in the air reacts with the lime leading to a decrease in pH over time and monitoring of the pH is therefore crucial during the treatment assuring that the pH does not reach below the level of sanitation.

Table 4: Treatment requirements for chemical treatment of wastewater products and manure. Main regulation is related to sewage sludge, with the exception of animal manure marked by*

Treatment	Temp.	Time	Other requirement	Regulation/ Country	Clasification
Liming pH 12	52°C (12 h)	72 h	drying >50% TS	USEPA	Klass A
	55°C	2 h		UK EC 2000	enhanced
	60°C	120 min		Norway	
pH 12.8	-	3 months		UK 2009 EC 2000 Denmark Germany	advanced
Ammonia treatment	-	1 week	2% urea, during salmonella outbreak*	Sweden	Manure treatment
Drying		>3 months		USEPA	Class B

Burned lime sanitisation is a much quicker treatment alternative as the CaO is very reactive and an oxidative, exothermic reaction occurs upon mixing. The treatment requires relatively large amounts of lime to be efficient. For reaching a temperature of 60°C in a sludge with 25% dry matter content, addition of 14% lime is required, leading to a final dry matter content of 40% (NORWAR, 2007).

Liming is a well-established method for sanitising treatment. The main factor for the treatment is its relatively high cost, due to large additions of lime required to reach high enough pH, Lime cost correspond to 4-5€ per person equivalent. Additionally, the working environment has to be controlled due to the high pH and oxidising effects of the burned lime.

Ammonia treatment is performed by using the well-known effect upon microorganisms from uncharged ammonia (Warren, 1962). The charged ammonia ion (NH_4^+) on the other hand is not toxic and can be used as fertiliser after the treatment. Therefore, the treatment leads to increased fertiliser value of the treated product. The ammonia treatment is the common effect found when storing urine from source separated systems. In blackwater system is it also possible to sanitise with the intrinsic ammonia of the system (Fidjeland et al., 2013). If the intrinsic ammonia is not enough in the material, additional ammonia can be added either via water solved ammonia or as urea (Nordin et al., 2009). Water solution with 25 % ammonia result in a rapid increase in the pH to above nine even at low addition rates (Ottoson et al., 2008). When adding urea, naturally occurring microorganisms degrades the urea enzymatically into ammonia and carbonate. The urea addition leads to a lower pH compared to the ammonia addition as the carbonate buffer the pH, and the addition reaches a pH of 8.8 and above after addition (Nordin, 2010).

Ammonia is a weak base, pKa=9.25 at 25°C (50% of the molecules are found in the uncharged form), the relationchip is according to the following equation.

$$NH_3\ (g)\ \text{"}\rightleftharpoons\text{"}\ NH_3\ (aq) + H_2O\ (l)\ \text{"}\rightleftharpoons\text{"}\ NH_4^+(aq) + OH^-(aq) \qquad (1)$$

The more uncharge ammonia (NH_3) found in the material the more efficient the treatment is. The uncharged ammonia is regulated by the concentration total ammonia and the equilibrium between the charged ion and the uncharged molecule is driven towards more uncharged ammonia by increased pH and increased temperature.

There is a non-linear correlation for the inactivation rate for ammonia concentration in relation to temperature. When increasing the temperature the inactivation rate increases faster. As a rule of thumb for inactivation of bacterial pathogens, e.g. *Salmonella* spp., the uncharged ammonia concentration needs to be at least 10 mM, indifferent of temperature. Compared to liming the pH of the ammonia treatment can be considerably lower as the main effect is the ammonia and not the pH.

The ammonia treatment is an efficient treatment that can be performed on demand, related to the use of the fertiliser. Important factor related to the ammonia treatment is that the treatment requires closed treatment facility, to avoid ammonia emissions. The enclosure can be performed by using plane silo plastic cover that has been tested in pilot scale for treatment of sewage sludge in Uppsala (Figure 1). The major difference when treating sewage sludge with ammonia, the material will be a full fertiliser, and not only a phosphorus fertiliser, and therefore be applied in the spring.

Figure 1: Ammonia treatment for sanitisation of sewage sludge in pile covered with plastic

The ammonia treatment is a new technology and the knowledge regarding the treatment is growing rapidly, and the treatment has been commercialised in the self-sanitising, single use, biodegradable toilet peepoo (Vinnerås et al., 2009). The treatment has also been tested in pilot scale for sewage sludge treatment in pilot scale treating batches of 65 ton and knowledge is available for full scale implementation. Additionally the treatment is used for sanitisation of contaminated manure and digestate from anaerobic treatment. The cost of the treatment is more or less regulated to the cost of ammonia as the investment cost is small and the treatment can be performed with available machinery e.g. normally used for composting or farm machinery.

5. Conclusion

The treatment requirements for different treatment alternatives vary a lot in different EU countries. This makes it complicated to generalise a treatment over the full EU.

The main aim with hygiene treatment is to reduce the risk of disease transmission. The more treatment the higher loss of plant nutrients while the risk for disease transmission decreases. These two factors has to be placed opposite to each other and evaluated regarding the nutrient content in the fertiliser and the risk for disease transmission.

References

Clemens, J., Vinnerås, B., Jönsson, H., Winker, M., Arnold, U., Mang, H.P., (2012) The potential contribution of NASS products on the fertilizer use and impact on greenhouse gas emissions in different countries.

Fidjeland, J., Magri, M.E., Jönsson, H., Albihn, A., Vinnerås, B. (2013) The potential for self-sanitisation of faecal sludge by intrinsic ammonia. Water Research, 1-10.

Nordin, A., (2010) Ammonia Sanitisation of Human Excreta, Dep. of Energy and Technology. Swedish University of Agricultural Sciences, Uppsala.

Nordin, A., Ottoson, J.R., Vinnerås, B. (2009) Sanitation of faeces from source-separating dry toilets using urea. Journal of Applied Microbiology 107, 1579-1587.

Nordin, A.C., Vinnerås, B. (2013) Combitreatment, with mmonia and heat, for fast ans secure sanitisation of blackwater. Manuscript.

Nyberg, K.A., Vinneras, B., Lewerin, S.S., Kjellberg, E., Albihn, A. (2011) Treatment with Ca(OH)(2) for inactivation of Salmonella Typhimurium and Enterococcus faecalis in soil contaminated with infected horse manure. Journal of Applied Microbiology 110, 1515-1523.

Ottoson, J., Nordin, A., von Rosen, D., Vinneras, B. (2008) Salmonella reduction in manure by the addition of urea and ammonia. Bioresource Technology 99, 1610-1615.

Sahlstrom, L., Aspan, A., Bagge, E., Danielsson-Tham, M.L., Albihn, A. (2004) Bacterial pathogen incidences in sludge from Swedish sewage treatment plants. Water Research 38, 1989-1994.

Warren, K.S. (1962) Ammonia toxicity and para H. Nature 195, 47-&.

Vinneras, B., Bjorklund, A., Jonsson, H. (2003a) Thermal composting of faecal matter as treatment and possible disinfection method--laboratory-scale and pilot-scale studies. Bioresour Technol 88, 47-54.

Vinneras, B., Bjorklund, A., Jonsson, H. (2003b) Thermal composting of faecal matter as treatment and possible disinfection method - laboratory-scale and pilot-scale studies. Bioresource Technology 88, 47-54.

Vinnerås, B., Hedenkvist, M., Nordin, A., Wilhelmson, A. (2009) Peepoo bag: self-sanitising single use biodegradable toilet. Water Science and Technology 59, 1743-1749.

Vinnerås, B., Nordin, A., Niwagaba, C., Nyberg, K. (2008a) Inactivation of bacteria and viruses in human urine depending on temperature and dilution rate. Water Research 42, 4067-4074.

Vinnerås, B., Winker, M., Clemens, J. (2008b) Non-metallic contaminants in domestic waste, wastewater and manures constraints to agricultural use. Internat. Fert. Soc., York, UK.

Authors

Björn Vinnerås, Annika Nordin

Swedish University of Agricultural Sciences

BOX 7032

SE-750 07 Uppsala, Sweden

Phone +46 (0)18 67 18 34

Email:bjorn.vinneras@slu.se

Conceptual principle for development of new end uses in recycled water schemes

Zhuo Chen, Huu Hao Ngo, Wenshan Guo

University of Technology, Sydney

Abstract

With a constantly growing population, water scarcity becomes the limitation for further social and economic growth. An increasing trend in water market is to consider recycled water as an essential component of integrated water resources management, as this approach can provide sufficient flexibility to respond to short-term needs and increase the reliability of long-term water supplies. The current application of recycled water is mainly limited to non-potable purposes, especially the ones involved with low human contact (e.g., irrigation, industry, gardening, toilet flushing and car washing). To meet the future water demands as well as attain the aggressive recycling goals formulated by the government, it is vital to consider new recycled water applications in both urban and rural areas. Consequently, this paper is to propose conceptual principles for exploitation and development of new end uses (e.g., household laundry, livestock use, and swimming pool). Some key issues such as water quality requirements, risk control measures and site specific conditions are discussed as well, which may hinder the implementation of new recycled water applications if handled improperly. The findings from this paper could provide fundamental information for the subsequent quantitative model construction, which in turn could further verify the feasibility of proposed end uses through various case studies.

Keywords: water scarcity; recycled water; conceptual principles; new end uses

1. Introduction

The current critical situations including the diminishing natural water resources, increasing water demand, deteriorated water quality, highly variable climate and environmental concerns, become the major driving forces for adoption of recycled water as a supplementary water supply. As for some developed countries, urban and residential recycled water schemes are developed rapidly, the amount of which are likely to be as high as or higher than that of agricultural irrigation schemes. High value end uses (e.g., groundwater recharge and indirect potable reuse) with potential close human contact are promising but still somewhat ambiguous due to strong public misgivings. Comparatively, in less developed countries, the major user of recycled water will continue to be the agricultural irrigation as recycled water is not only a supplementary water resource but also provides additional nutrients for irrigation. There would be a tendency in recycled water market towards higher level of treatment only if the cost of membrane treatment processes fall. Besides, decentralized treatment systems would be favoured in both urban cities and small towns due to the simplicity, flexibility and cost effectiveness. Moreover, direct potable reuse (DPR) schemes could be considered in arid and semi-arid regions in the near future owing to the successful cases in Namibia and South Africa. According to the recent trends, new recycled water end uses might be promising and should be exploited encouragingly (Chen et al., 2013).

2. Potential for the development of new end uses of recycled water

2.1 Recycled water in household laundry

Generally, household laundry accounts for 15-20% of household water usage and is regarded as the second largest indoor user of water. However, the water consumption for laundry in different households may vary substantially due to the variety of washing machine types, number of washes, wash temperatures, load sizes, etc. In Europe and Turkey, most of the households employ the state-of-art front loading washing machines which consume around 60 litres of water per wash and use electricity to heat up water internally by integrated heating rods. While in Australia, North America and Asia, top loading machines are widely adopted which consume over 100 litres of water per wash and the water normally comes from external cold and/or warm water taps that is not heated by the washing machine further. Due to the traditional laundry habits and practices, low wash temperatures have been widely adopted in these countries (Pakula and Stamminger, 2010). Consequently, although European households use significantly less amount of water than the households in other regions, they require additional energy to heat up water from cold water tap. Overall, more than 9.9 kilolitres (kL) of fresh water could be saved per household per year worldwide if recycled water could be reticulated to the cold water input tap to the washing machine. Moreover, the life cycle unit cost of the proposed new laundry use scenario might be financially viable, when considering the total resource and operating/maintenance cost perspectives. Besides, the water authorities will also benefit from this new end use as the treated recycled water could be utilized effectively rather than being directly discharged to the environment, resulting in higher revenue from increased recycled water demand (Bertone and Stewart, 2011).

2.2 Recycled water in livestock feeding and servicing

Currently, the amount of water used in livestock industry is relatively high and there is a need to increase water supply in multiple processes, from feeding, servicing to production. In Australia, livestock farming activities only utilize 5,622 ML/year of recycled water at present, compared with 612 and 288 GL/year from self-extracted and distributed water sources respectively (ABS, 2012). Hence, there would be a great potential to further exploit livestock drinking and servicing as new recycled water end uses in non-metropolitan areas. More specifically, although livestock are able to absorb water contained in feedstuffs and metabolic water produced by oxidation of nutrients, drinking water is the prime way to meet their daily water requirements. However, water needs vary because of the discrepancies of the animal species, breed, age, weight, level of dry matter intake, physical form of the diet, water quality, temperature of the supply water, ambient temperature and the farming system. In warm and dry conditions, water requirements can be extremely high due to increased water losses (Chapagain and Hoekstra, 2003; FAO, 2006).

Additionally, livestock servicing also require a large amount of water which can be seven times higher than drinking water needs, to clean the livestock production units, wash animals, cool the facilities, animals and their products as well as discharge the wastes. Compared with grazing systems, service water consumption in industrial systems is generally higher owing to extra cooling and cleaning purposes of facilities. Hence, if the recycled water can be properly treated to a standard that is appropriate for livestock production, considerable freshwater savings would be achieved, especially in intensive farming systems. While this new end use has not been extensively discussed globally, some areas such as the State of Victoria, Australia, have already formulated guidelines where the Class A recycled water with tertiary treatment and pathogen reduction is recommended for general livestock (SGV, 2009).

2.3 Recycled water in swimming pool

Aquatic centres and swimming pools are major public facilities that provide significant benefits in terms of community development, sport, health and fitness to local residents. As they require a large amount of water and energy to operate and maintain, a number of public pools have been closed during the drought conditions. If no action were taken to mitigate inevitable water shortages in the future, there would be higher risks of closure for more pools in extreme weather situations, affecting the aquatic and recreational industry. The main water consumption categories of a typical aquatic centre are depicted in Figure 1.

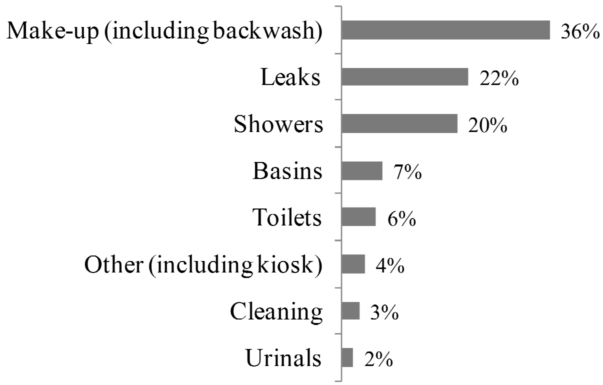


Figure 1: Water use breakdown of a typical aquatic centre (Modified from Sydney Water, 2011)

While strategies such as dual flush toilet systems, water saving and flow regulation devices in shower heads, and pool covers are commonly reported approaches being successfully implemented in many newly constructed aquatic centres, there will be a great potential in water saving and reuse when adopting measures on treating backwash water for use as pool make-up water. To control the risks under low levels, it is advisable to introduce advanced treatment technologies such as reverse osmosis (RO) and conduct frequent monitoring and maintenance. Notably, a lack of understanding may hinder the implementation process or cause the systems remain dysfunctional for a period of time. Hence, it is essential to ensure that adequate training, information, manuals and some level of feedback have been obtained on how to operate and maintain the strategy efficiently and effectively. There are several successful applications of recycled backwash water in Australian public aquatic centres, including pools in Penrith and Ryde city councils, Sydney, Victoria, but the documented information is still quite limited (Hazell et al., 2006).

3. Proposed methodology for assessing new end uses of recycled water

Based on the above-mentioned new end uses of recycled water, a qualitative feasibility analysis can be conducted in the preliminary stages of decision making, which is to identify the critical factors associated with the successful implementation of the schemes, including the project's strengths, weaknesses, opportunities and threats.

1) ***Strengths and weaknesses***. The strengths of new end uses mainly lie in large and constant water consumption whereas the weaknesses may include: close human contact, potential high risks to health, a lack of comprehensive quantitative assessment, and additional cost for pipe installation and/or treatment facilities.

2) ***Opportunities and threats***. The opportunities involve limited information on water reuse, potential significant freshwater savings and reduced wastewater discharges, available treatment technologies, while the threats might include concerns, suspicion, distrust and discomfort from householders, farmers and customers, and insufficient systematic management and training.

After that, the quantitative analysis of the proposed new end uses of recycled water should be performed. The procedures are as follows (Chen et al., 2012):

i) Consideration of specific management alternatives related to each new end use. Firstly, a baseline scenario should be included which can be regarded as a hypothetical reference case. In new end use(s) evaluation, the baseline presents the situation that recycled water use activities would occur in the absence of proposed new end uses (laundry, livestock using or swimming pool). Secondly, some scenarios may embody the selection of different equipment and/or facilities (e.g., the adoption of top or front loading washing machine type in household laundry, the use of grazing or intensive farming system in livestock production industry and the installation of water efficient facilities in swimming pools). Besides, some scenarios may also be associated with the adoption of different treatment technologies to achieve varied recycled water quality. Apart from tertiary treatment employing microfiltration (MF) and ultraviolet disinfection, more advanced techniques such as MF-zeolite system, MF-activated carbon system and MF-reverse osmosis system are supposed to be discussed to further improve the recycled water reliability and community acceptance.

ii) Selection of key criteria that might affect the implementation of new end uses. As can be seen from Figure 2, to ensure comprehensiveness and objectiveness of the assessment, it is advisable to take into account of relevant technical, environmental, social and economic aspects of alternatives appropriately in the decision making procedure. Each key index contains several sub-indexes that need to be measured via either qualitative or quantitative approaches.

iii) Application of multi-criteria analysis (MCA). The targets of adopting MCA methodology are to investigate the tradeoffs among these selected multiple conflicting criteria, and obtain rankings of different management alternatives under certain mathematical algorithms. From the computerized MCA simulation which consists of scoring, weighting and aggregation processes, the least preferred options towards one/several end use(s) could be quickly eliminated whereas the superior alternatives can be further discussed.

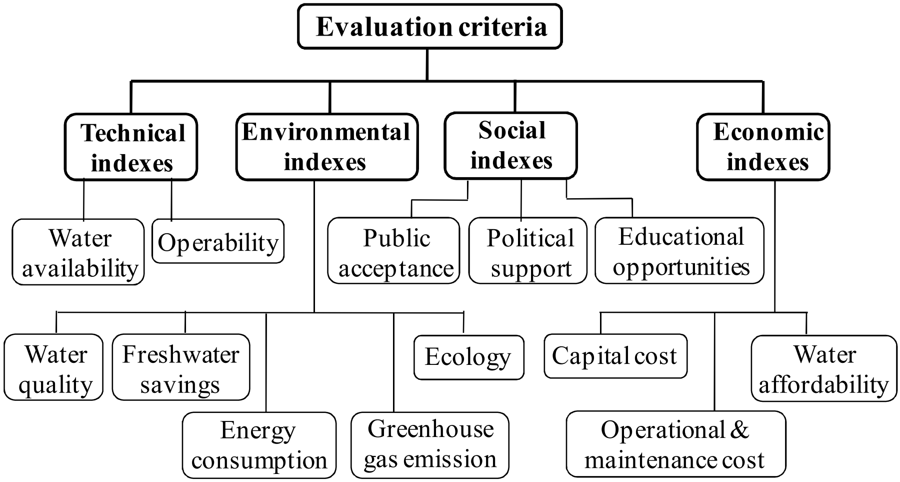


Figure 2: Evaluation criteria for comprehensive assessment of recycled water new end uses

iv) Recommendation of preferred option(s), review and reporting. At management stage, a detailed assessment report can be presented to relevant government departments, which should include the major strengths and barriers regarding the new end use strategy implementation and expansion, together with periodic review and evaluation plans in future operational stages.

4. Conclusions

This paper identified the potentials for the development of three recycled water new end uses, household laundry, livestock drinking and servicing and swimming pool, in future water use market. Based on the strengths of these new applications, the sound conceptual decision analytic framework and methodology have been developed to facilitate the establishment of optimal management strategies. These could provide effective guidance on the future end use studies within a larger context of the technical, environmental, social and economic status in decision-making.

Acknowledgement

This work was funded by Australian Research Council (ARC) Industry Linkage Grant (LP100100494). The authors acknowledge the support from Port Macquarie Hastings Council, City West Water, Gold Coast Water and Sydney Olympic Park Authority.

References

ABS (Australian Bureau of Statistics) (2012). Water Account Australia 2010–11.

Bertone, E. and Stewart, R. A. (2011). Framework for enhancing the supply-demand balance of a tri-supply urban water scheme in Australia. Water, 3, 976-987.

Chen Z., Ngo H. H., Guo W. S., Listowski, A., O'Halloran, K., Thompson, M. and Muthukaruppan, M. (2012). Multi-criteria analysis towards the new end use of recycled water for household laundry: A case study in Sydney. Science of the Total Environment, 438(1), 59-65.

Chen, Z., Ngo, H. H. and Guo, W. S. (2013). A critical review on the end uses of recycled water. Critical reviews in Environmental Science and Technology, 43, 1446-1516.

Chapagain, A. K. and Hoekstra, A. Y. (2003). Virtual water flows between nations in relation to trade in livestock and livestock products. Value of water research report series No. 13.

FAO (Food and Agriculture Organization). (2006). Part V: Livestock’s role in water depletion and pollution. In: Livestock’s long shadow, environmental issues and options.

Hazell, F., Nimmo, L. and Leaversuch, P. (2006). Best Practice Profile for Public Swimming Pools – Maximising Reclamation and Reuse. Royal Life Saving Society, Perth, Western Australia.

Pakula, C. and Stamminger, R. (2010). Electricity and water consumption for laundry washing by washing machine worldwide. Energy Efficiency, 3, 365-382.

SGV (State Government Victoria) (2009). Reclaimed water use in livestock production. In: Recycling and waste management.

Sydney Water (2011). Best practice guidelines for water management in aquatic leisure centres.

Authors

Zhuo Chen, Huu Hao Ngo, Wenshan Guo*

Centre for Technology in Water and Wastewater

School of Civil and Environmental Engineering

University of Technology Sydney, Sydney, NSW 2007, Australia

**Corresponding author, Email: h.ngo@uts.edu.au, Tel: +61 (2) 95142745, Fax: + 61(2) 95142633*

(Comparative) Technical, environmental and economic assessment of Phosphorus recycling technologies from waste water

Lukas Egle, Helmut Rechberger, Matthias Zessner

Vienna University of Technology

Abstract

Phosphorus (P) is a finite and non-substitutable resource, essential to sustain high levels of agricultural productivity, but also responsible for environmental problems, e.g. eutrophication. The developed Austrian P budget confirms on the one hand the dependence of mineral P fertilizers application (2 kg $cap^{-1}yr^{-1}$), but it highlights on the other hand considerable but often unexploited P-load in municipal waste water (~1 kg $cap^{-1}yr^{-1}$). Numerous recycling technologies have been developed and partially implemented over the past years to recycle P from different sources of a waste water treatment plant. This work is taking the approach to develop a methodology for a comparative technical, environmental and economic assessment of 18 selected P-recycling technologies and giving decision makers all necessary information for possible future implementation. Additionally, the technologies will be assessed by taking into account the whole process chain to show the results from a macro-economic point of view. The results show, that there is no final indicator to assess the complex and various technologies. In fact, the results from the numerous assessment criteria create a picture, which describes a recycling technology overall.

1. Introduction

Regarding the important role of P-containing mineral fertilizers on total global P supply (80–90%), it is obvious that future demand will be driven by development of the agricultural sector. Development in agriculture on the other hand will be forced by prognosis of population growth and changes in diet due to rising living standards in emerging and developing countries (Cordell et al., 2011). Consequently P-demand will rise in agriculture. But on contrary to the prognosis of rising demand faces an exhaustible and finite resource. Austria, as other European countries which have no P-deposits of their own, are fully dependent on P-fertilizer imports. Looking at national P-budgets on the other hand shows the large but often unexploited P-potential in waste water (~1 kg $capita^{-1} year^{-1}$) and subsequently in different streams of a waste water treatment plant (WWTP). Exemplarily occurring municipal sewages sludge in Austria offers a theoretical substitution potential of about 40% of annually applied mineral P-fertilizer (Egle et al., 2013). Similar numbers can be found for Germany (Gethke-Albinus, 2012) and Switzerland (Binder et al., 2009). Direct sewage sludge application in agriculture is an appropriate and most simple method of P-recycling. But due to potential environmental risks, namely heavy metals (HM), persistent organic pollutants (POPs) and hygienic, acceptance on direct utilization of sewage sludge is frequently low or decreasing in many countries, as well in Austria.

Furthermore, from the view of a large scaled waste water treatment operator, the challenges of economic and safety disposal are necessary but are often not be achieved by direct sludge application. Consequently the most valuable nutrient phosphorus (P) is presently irretrievable lost as alternatives focus on incineration and/or disposal of sludge or ashes to landfill. Thus, several technologies have been developed and occasionally large scale implemented to recover on the one hand P on a high level from different waste streams and on the other hand produce a plant available product with reduced environmental risks. Potential streams in and after a waste water treatment plant are effluent (E), sludge water (SW), sewage sludge (SS) or sewage sludge ash (SSA) (Figure 1). These streams differ strongly in volume, P-concentration, the consistence of P (diluted, biologically and/or chemically bound) and the characteristic of the source (liquid, liquid/solid, solid). Due to the varying characteristics of the P-source, recycling technologies vary in plant and process engineering, complexity, resource and energy demand. But often data on recycling potential, resource demand, path of heavy metal, effects on the environment and costs are not available. This work is taking the attempt researching all relevant data, developing an appropriate method allowing comparative integrated evaluation of selected technologies (Table 1) regarding technological, ecologic and economic criteria. Thus, 18 different technological approaches, covering the brought field of P-recycling have been selected, to apply the developed method.

In order to simplify the comparison of the selected technologies, they are grouped by their technical approach:

Crystallisation or ***precipitation***: Ostara®, DHV Crystalactor®, P-RoC, PRISA, AirPrex® (sewage sludge); ***Ion-Exchange***: REM-NUT®; ***Wet-chemical***: Seaborne®, Stuttgarter Verfahren; ***Wet-oxidation***: AquaReci®, PHOXNAN; ***Metallurgic***: MEPHREC®; ***Thermo-chemical***: Ash Dec®; ***Wet-chemical*** (***extraction***): LEACHPHOS®, PASCH, SESAL-Phos; ***Wet-chemical*** (***mixing***): RecoPhos®, Fertilizer Industry; ***Thermo-electric***: Thermphos®

Table 1: Selected P-recycling technologies for integrated assessment

Sludge Water/Effluent	Sewage sludge (SS)	Sewage sludge ash (SSA)
Ostara® (2)	AirPrex® (3)	Direct SSA application (7)
DHV Crystalactor® (2)	Seaborne® (4)	Ash Dec® (now Outotec®) (7)
P-RoC (2)	Stuttgarter Verfahren (4)	PASCH (7)
PRISA (2)	PHOXNAN (5)	LEACHPHOS®
REM-NUT® (1)	AquaReci® (5)	RecoPhos® (7)
	MEPHREC® (6,7)	SESAL-Phos (7)
		Thermphos (P_4 production) (7)
		ICL (Fertiliser Industry) (7)

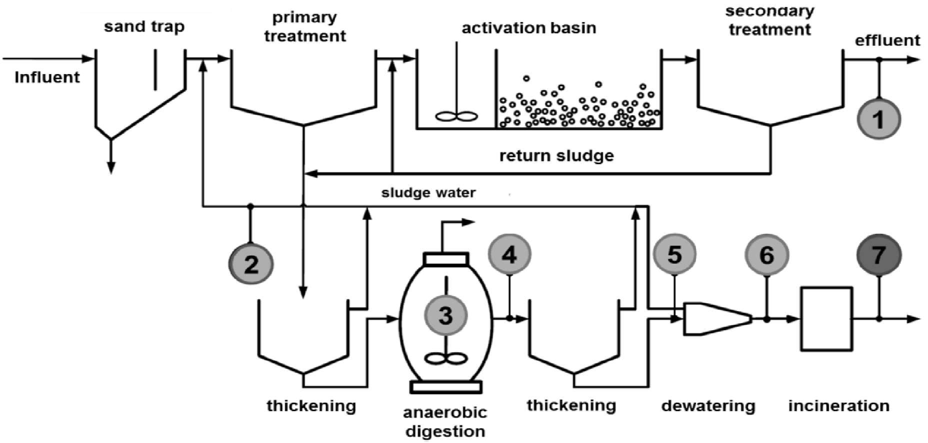


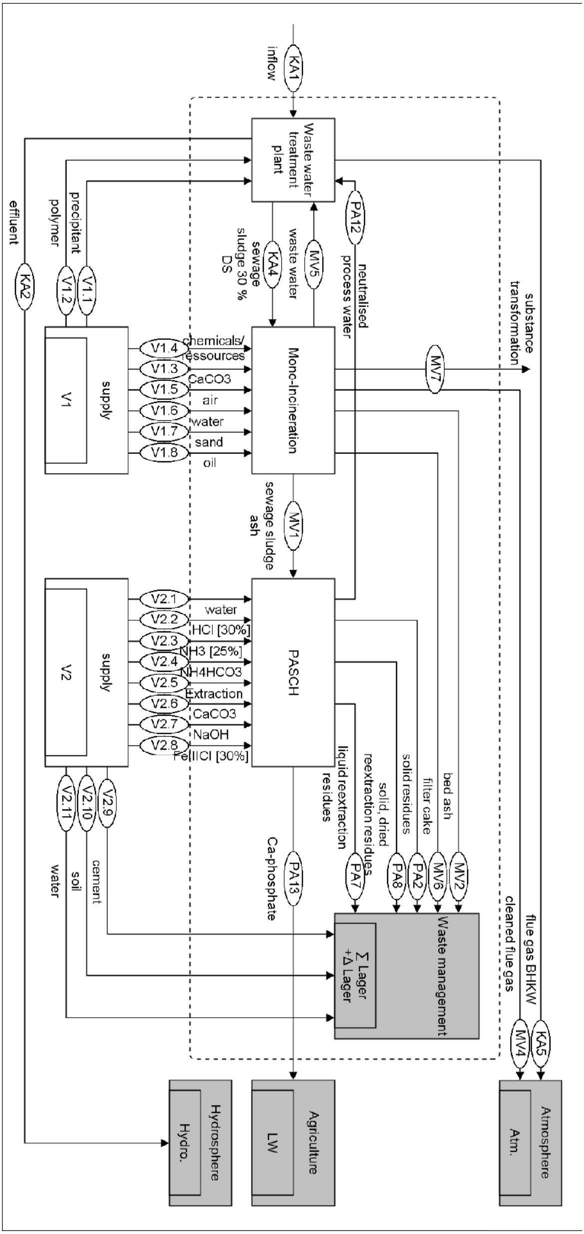
Figure 1: Potential P-recycling streams (Montag, 2008 modified)

2. Methodology

Development of a “modular system” with defined reference processes and the selected P-recycling technologies is the basic system for comparable evaluation. Thus, a reference waste water treatment plant with a load of 100,000 population equivalents (PE) (=65,700 kg P) and reference sludge treatment processes as thickening, anaerobic treatment, dewatering, mono-incineration and landfill are selected. This is necessary due to the different possible operational places of recycling technologies: directly at the WWTP or after different stages of sludge treatment options. So the complexity of a technology, possible positive or negative effects to the waste water treatment process and occurring by-products are considered. Figure 2 shows the defined material flow analysis model for the whole process chain from the reference waste water treatment until final disposal of occurring waste regarding the recovery technology PASCH after mono-incineration. For all reference processes as well the recycling process transfer coefficients are defined. On this basis material flow analysis (MFA) using software STAN (subSTance flow ANalysis, Cencic and Rechberger, 2008) is applied to detect the recycling potential of a technology (P), the path of direct emissions of heavy metals (As, Cd, Cr, Cu, Hg, Ni, Zn) and micro pollutants (if data is available) to atmosphere, receiving waters, soils and final disposal systems (Brunner and Rechberger, 2004). Simultaneously MFA for heavy metal shows potential elimination rate during the recycling process. Material and energy flow analysis in combination with an LCA database (GEMIS) is applied to create a life cycle inventory (GEMIS, 2013). Indirect gaseous (CH_4, CO, CO_2, HCl, HF, NH_3, NO_3, N_2O, SO_2) as well as heavy metal emissions and cumulative energy demand (CED) are considered.

Aim is on the one hand the evaluation of the recycling process itself and on the other hand the evaluation of the whole process chain from waste water treatment, application of secondary fertilizers and final disposal of occurring wastes. Besides direct and indirect emissions, an important part of the ecologic assessment is the characterization of the final products. Nutrient- and pollution content, solubility, fertilizing effect and beyond the handling of the products and its possibility for direct agricultural application are considered. To evaluate the pollution content the method of toxic equivalent model and self-created reference soil method is applied. Important criteria for successful future implementation are costs. Therefore, this work considers detailed cost analysis by using the calculation methods of annual costs (running costs, cost of capital) and capital value. Possible savings in waste water treatment due to the recycling process and revenues by the end product are taken into account. Cost calculations will be supplemented by sensitivity analysis (varying annual cost, different P-content of recycling sources) and different WWTP capacity (from 100,000 PE to 500,000 PE). Assessing recycling technologies from sewage sludge ash, recycling plans with a capacity of at least 15,000 t ash yr^{-1} are considered. Cost calculation is done both for the recycling process and for the entire process chain. For comparative technology assessment ecologic and economic data output is related to 1 kg P recovered (kg $P_{rec.}$) respectively 1 population equivalent and year (PE yr^{-1}).

Figure 2: Material flow analysis (MFA) model for reference situation and the recycling technology PASCH



3. Results

One of the key findings is that due to complexity of the considered potential recycling streams and recycling technologies, as well as possible effects to the total system, there is no final assessment indicator respectively final approach for P-recycling from waste water. Rather, the selected individual parameters result in a total picture for each recycling technology. The most relevant results will be shown in the following capita.

3.1 Recycling potential

With detailed MFA for P, the recycling performances of all technologies have been assessed, regarding the performance of the technology itself and as well with regard to WWTP influent. Figure 4 shows exemplarily the recycling performance for the wet-chemical PASCH process (a) and the process included in the whole process chain (b).

With P-recycling technologies up to 90% of P in sludge water is recoverable, but with respect to WWTP inflow the recycling potential is quite low (15–max. 40%). With respect to a great recycling extent of P in waste water these technologies are unsuitable but may have operational benefits as e.g. avoidance of MAP incrustations and lower P-back contamination. The recycling potential of technologies from sewage sludge differs quite strongly. With wet-chemical processes the recycling potential related to the WWTP inflow is <50% whereas the potential with wet-oxidation process is on the same level (PHOXNAN) or slightly higher (AquaReci®). With the metallurgic MEPHREC® process recycling quote related to WWTP is up to 70%. Highest recycling potentials can be reached with technologies which address mono-incinerated sewage sludge ash (60–85% related to WWTP influent). The recycling potential is directly connected to heavy metal depletion. Technologies without depletion show recycling potential of up to 100% with respect to the ash and about 80–85% related to WWTP influent (Ash Dec®, RecoPhos®, Fertilizer Industry, Thermphos®). In contrast the wet-chemical technologies LEACHPHOS, PASCH and SESAL-Phos reach a lower recycling potential of 60–70% related to WWTP influent. For comparison direct sewage sludge and sewage sludge ash application to agriculture are shown in addition in Figure 4.

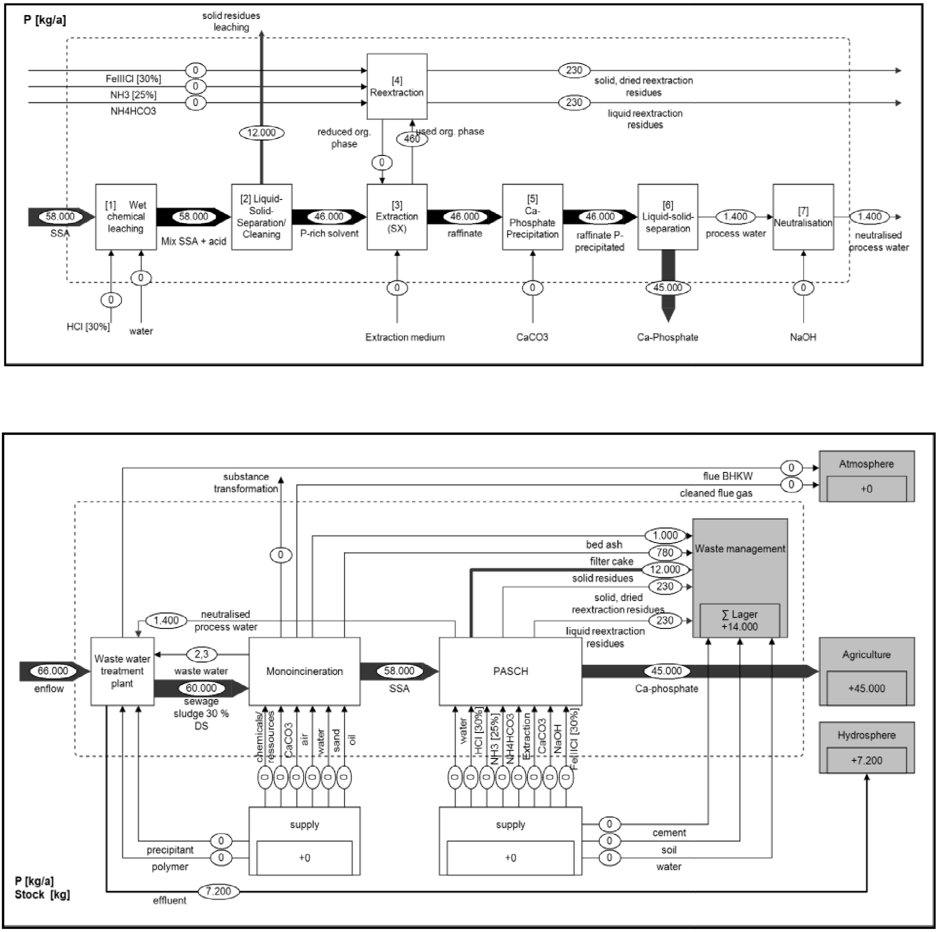


Figure 3: Material flow analysis (P) for the PASCH process: a) only PASCH, b) whole process chain

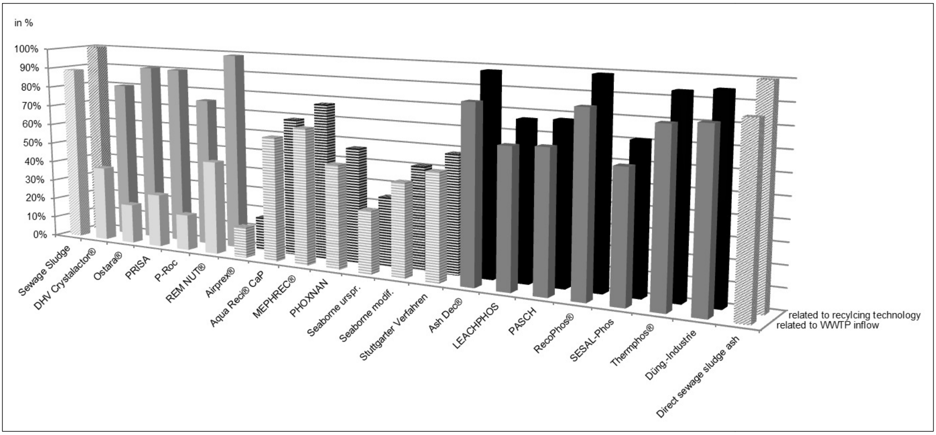


Figure 4: P-recycling potential related to recycling technology and to WWTP inflow

3.2 Performance of heavy metal and persistent organic pollutant removal

Due to the potential environmental risks, namely heavy metals (HM) and persistent organic pollutants (POPs), further purpose of the recycling technology is their depletion to achieve a secondary fertilizer with reduced environmental risks. For P-recycling in sludge water, HM and POPs aren't relevant. Technologies from sewage sludge and sewage sludge ash show quite different results. Different technological approaches in sewage sludge (precipitation, complexation, nanofiltration, alkaline leaching) show high HM removal performances. Due to the complex HM removal processes the recycling potential can be reduced significantly. Persistent organic pollutants are negligible for almost all technologies, except for the wet-chemical approaches from sewages sludge, but with concentrations significantly below the fertilizer ordinance. The different approaches in sewage sludge ash show nearly fully (PASCH, SESAL-Phos, Thermphos®) partly (Ash Dec®) or even no HM removal (RecoPhos®, Fertilizer Industry, direct SSA). Obviously there is a direct correlation between recycling potential and efficiency regarding heavy metal removal.

Therefore, the selection is about technologies with almost total HM removal but lower recycling potential (60–70%; LEACHPHOS®, PASCH, SESAL-Phos) and technologies with partly or even missing HM removal but very high recycling potential (98–100%; Ash Dec®, RecoPhos®, Fertilizer Industry). Figure 5 shows exemplarily the path of Copper on the one hand for a technology itself (PASCH process) and on the other hand over the whole process chain (Figure 6). With the MFA over the whole process chain, the fate of P and selected heavy metals to landfill, hydrosphere, agriculture and/or atmosphere can be clearly shown. Exemplarily the path is shown for Ostara (sludge water), Seaborne® (sewage sludge) and the two technologies PASCH and RecoPhos® to recycle P from sewage sludge ash.

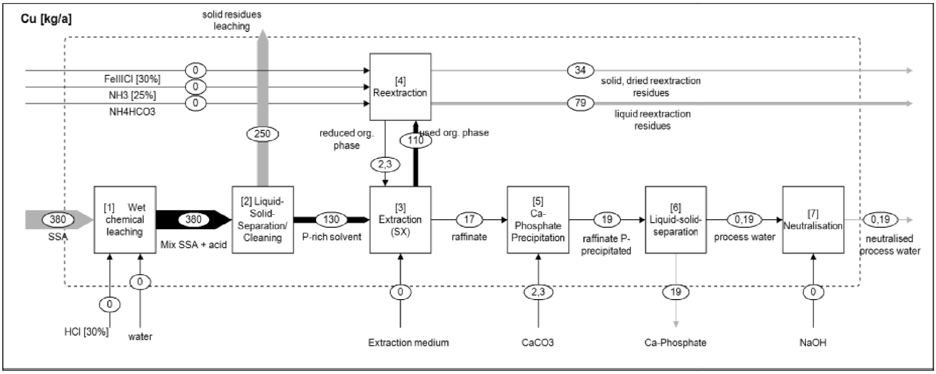


Figure 5: Path of Copper within the PASCH process

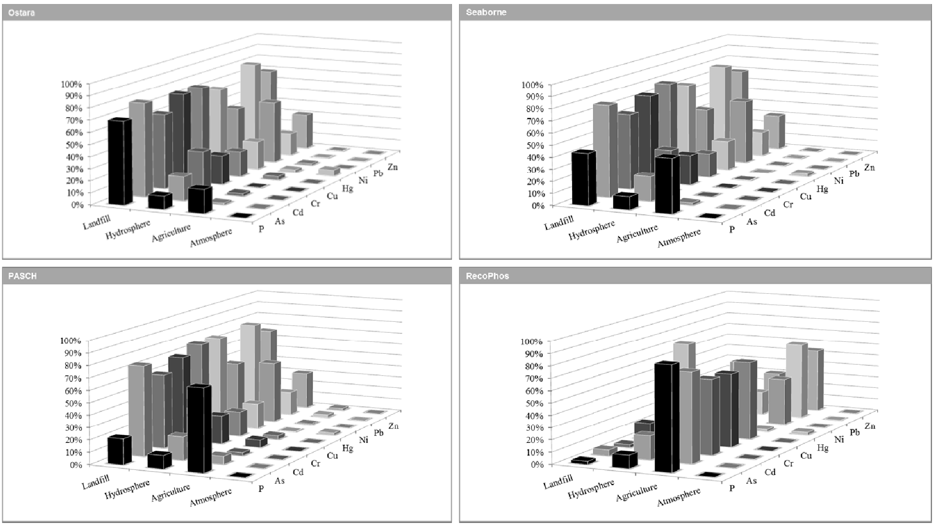


Figure 6: Path of P and selected HM for Ostara®, Seaborne®, PASCH and RecoPhos®

3.3 Costs

For future implementation the costs are one of the most essential criteria and therefore have been studied in great detail. Figure 7 shows annual cost for recycling technologies expressed as €/kg P_{rec}. and €/PE yr^{-1} without taking into account any savings or revenues. The bubble size indicates the recycling potential with regard to the waste water treatment inflow of the defined reference WWTP (max. 0.66/PE yr^{-1}). The cost calculation for the technologies from the sludge water/effluent and sewage sludge is based on a WWTP with a capacity of 100,000 PE (1 Mio. PE for MEPHREC®). For recycling technologies from ash, the capacity needs to be significantly higher, otherwise costs would explode. Therefore, the calculations are on basis of an annual performance of 30,000 t ash (~3.5 Mio. PE yr^{-1}).

3.3.1 Annual Cost

The costs for recycling technologies from sludge water are about 6 to 10 €/kg P or 0.8 to 2 €/PE yr^{-1}. The detailed cost analysis shows, that costs are mainly driven by the high investment cost for e.g. the crystallization reactor. By implementing such a reactor on treatment plants costs can be reduced significantly (up to -50% for 200,000 PE). By taking into account possible savings (reduction of P-back contamination, avoiding MAP incrustations) and revenues from the produced fertilizer these technologies may operate economically.

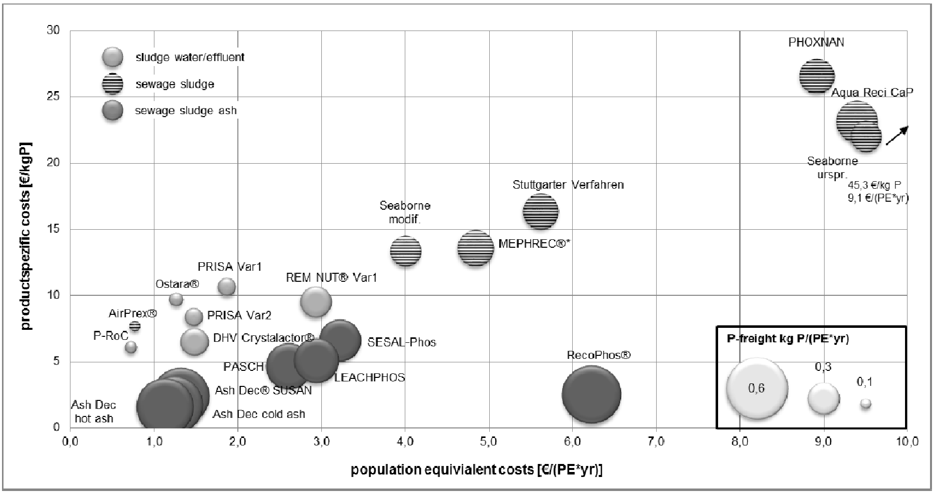


Figure 7: Annual cost without savings and revenues

Recovering phosphorus from sewage sludge is more expensive. E.g. the costs for 1 kg P with the wet-chemical processes is from 9 to 16 €/kg P. These costs are dominated by the chemicals (e.g. acids, caustics) and will not significantly reduce if up-scaled. The costs for the wet-chemical processes as Aqua-Reci® and PHOXNAN are outstandingly high (23–27 €/kg P). But taking into account revenues as e.g. by using the heat potential of the sludge and the value of the product, costs will decrease dramatically. Furthermore, beside the produced P-fertilizer, output is a disposable inert waste. Thus, further treatment of e.g. sludge is not necessary. The benefits will be shown within the calculations for the whole process chain. Similar conclusions were made for the MEPHREC® process. Cost for the wet-chemical processes to recycle P from sewage sludge ash and remove heavy metals significantly are around 5–7 €/kg P. Depending on the scenario, the annual cost for the Ash Dec® process with about 2 €/kg P is quite low. Similar results can be shown for the RecoPhos® process. The cost for using the ash as a secondary resource to substitute phosphate rock in Fertilizer Industry or the Thermphos® process are not shown in this figure. The assumption is that the ash is used in existing plants and therefore only the annual cost need not to be calculated for this two options. In this case, the costs are about 1 respectively 2 €/kg P for the Fertilizer Industry and the Thermphos® process (Figure 8).

3.3.2 Breakdown of cost

To get a deeper insight to the processes and saving potential the costs have been divided into capital costs, costs for maintenance, energy, chemicals, personal, miscellaneous and disposal of occuring wastes. Exemplarily the results for the recycling technologies using sewage sludge ash (Figure 8) show a quite different cost structure, even for similar recycling approaches. For example the wet-chemical processes PASCH and SESAL-Phos show dominating chemical cost and low capital cost whereas LEACHPHOS show comparatively high capital costs. Looking at the industrial processes of Fertilizer Industry and Thermphos®, costs are dominated by chemicals (sulfuric acid) respectively energy (coke and electricity).

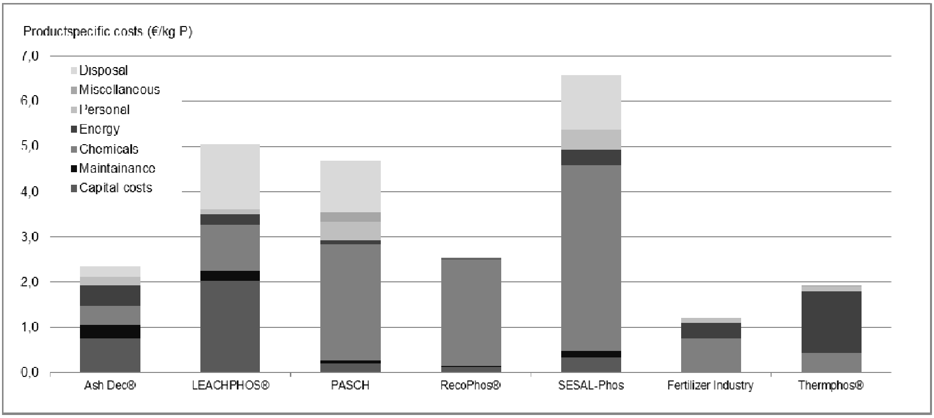


Figure 8: Breakdown of costs for recycling technologies form sewage sludge ash

3.3.3 Annual cost with possible savings and revenues

Taking into account possible savings and revenues is quite challenging due to missing full scale implementations. Hence, the assumptions are associated with high uncertainties. For recycling technologies from sludge water savings are possible by reduced back-charge of P (calculated by fictive savings of iron precipitants) and avoidance of MAP-incrustations (reduced maintenance costs). Together with revenues from product sale (calculated by the nutrient content of the final product and the market price of each nutrient) annual costs could have been reduced by over 50%. This reduced costs show the optimal scenario but in fact the costs will be somewhere in the fluctuation range of the annual costs without revenues and savings and the optimized annual costs.

With wet-oxidative technologies the energy potential of sewage sludge can be used by producing heat. In case of existing consumers the produced heat will be considered as revenues. Thus the annual cost decrease significantly (PHOXNAN, 9 compared to 27 €/kg P) or show even profit in case of the implementation of the AquaReci® process. Same results can be shown for the metallurgic MEPHREC® process, but only if produced heat is actually used (from 14 to 0 €/kg P respectively low profit). To determination costs for these technologies, high uncertainties need to be considered necessarily. Compared to the wet-oxidation and metallurgic approaches, possible cost savings for wet-chemical approaches as Seaborne® and Stuttgarter Verfahren are comparatively low. Reduced solid contend due to the acidification of sewage sludge and simultaneous recycling of iron for P-precipitation in the main stream process (Stuttgarter Verfahren) have been taken into account. Nonetheless annual cost of 9–11 €/kg P are still remarkable high. For the recycling technologies from sewage sludge ash but as well for sewage sludge in general, the question need to be asked, if the operator acts as a waste disposal contractor or not. This determines whether revenues due to ash take over need to be considered. On contrary, with changing market situation and rising demand for a P-rich ressource like sewage sludge ash, cost could arise for the operator. To consider both scenarios, no revenues or cost are assumed within the cost calculation.

By taking into account revenues and savings for the wet-chemical approaches on sewage sludge ash, costs can be reduced up to 50% (PASCH and LEACHPHOS®). Depended to the value of the decontaminated ash, achievement of profit is possible for Ash Dec® technology. Figure 9 shows the results with maximum revenues, calculated by the nutrient content of the decontaminated ash and its market price (monetary value: ~230 €/t ash). Actually the ash has hardly any value (~1 €/t ash) and therefore the here displayed profit situation is not plausible. In comparison the value of the RecoPhos® and Fertilizer Industry product corresponds to the monetary value respectively market price. Therefore, the results for RecoPhos® with low costs (0–0.3 €/kg P) respectively profit is very likely. Profits can be assumed as well for the Fertilizer Industry.

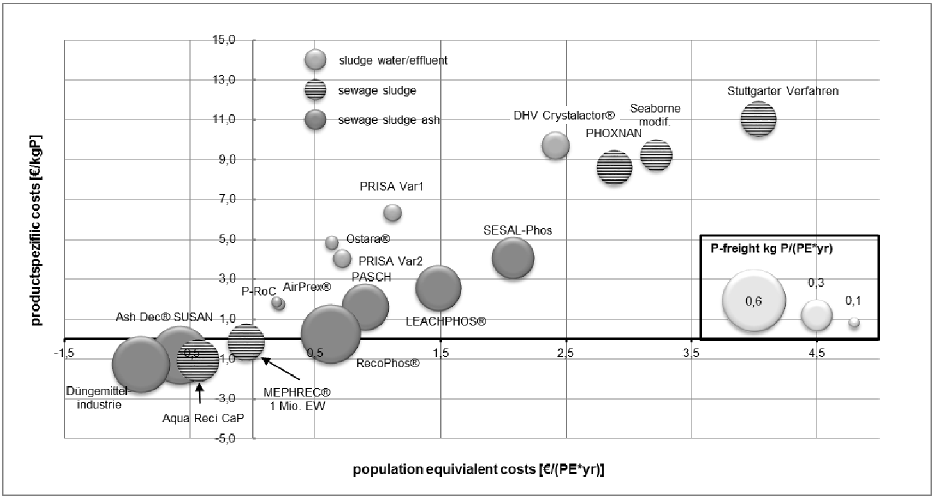


Figure 9: Annual cost with possible revenues and savings

3.3.4 Costs for the whole process chain

To have a look on the real costs from the view of national economy the whole process chain needs to be considered. Figure 10 demonstrates the costs for a recycling technology in case of implementing in the existing system of waste water management, sludge treatment and waste disposal. Again the calculations for the sludge water and sewage sludge technologies are made for a capacity of 100,000 PE respectively 30,000 tons for technologies from sewage sludge ash.

In case of the implementation of technologies in sludge water the additional cost are between 0.4 and 1.4 €/PE yr^{-1}. Hence, the additional costs are about 10% to the current system to recycle about 20–30% of P from waste water. As shown in chapter 4.3.3 the wet-oxidation and metallurgic approaches from sewage sludge show remarkable high fluctuation. Furthermore, with respect to the whole process chain, sewage sludge is transferred to an inert ash respectively slag for which direct deposition (e.g. landfill) is feasible. Therefore, further costs for e.g. incineration need not to be considered and positive economic effects are possible. But Figure 10 shows high fluctuation for these technologies and therefore does not allow making any reliable interpretations. Additional costs for the wet-chemical approaches from sewages sludge are about 30–40% to recovery around 40% of P from waste water.

Based on the scenario of “direct ash application” the additional costs for mono-incineration compared to reference co-incineration are shown (+0.5 €/PE yr^{-1}). For the wet-chemical approaches from sewage sludge ash additional costs are about 30% to recycle up to 60% of waterborne P. The additional costs for thermo-chemical treatment of the ash are about 10%. High uncertainties are assumed due to the unknown revenues of a decontaminated ash. Most likely the additional cost will be +20%, because the final products has hardly any value (1 €/t ash). For the scenario RecoPhos® and the Fertilizer Industry additional cost are about 1–1.5 €/PE yr^{-1}. Due to the high achievable price for the final products, costs are on the lower level of the fluctuation rate (1 respectively 0.5 €/PE yr^{-1}). These are the lowest cost compared to other recycling technologies and show at the same time the highest recycling potential of about 80–85% of P in wastewater. Furthermore a secondary fertilizer is produced, which is fully plant available. Disadvantage is the missing depollution of heavy metals.

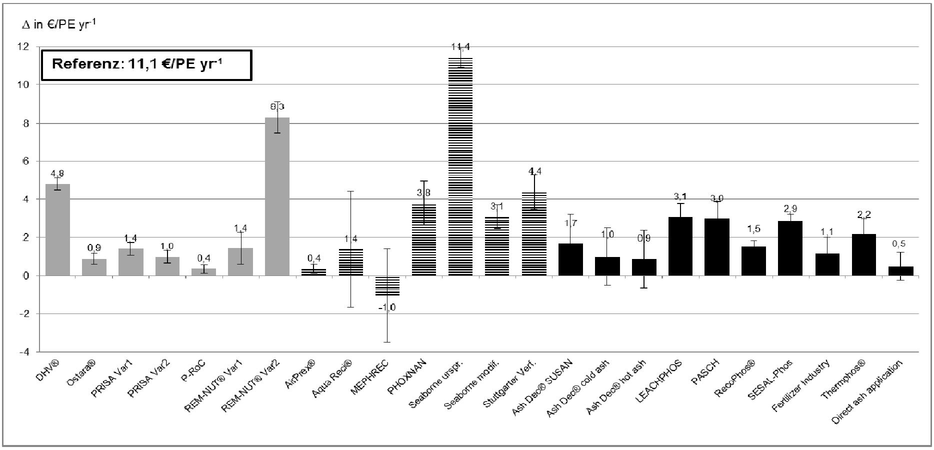


Figure 10: Additional or reduced costs for P-recycling technologies over the whole process chain (€/PE yr^{-1})

Same calculations were made for the costs related to the phosphorus recycling potential of the different technologies. Quite surprising is the fact that the additional cost to recover 1 kg P from sludge water by e.g. crystallization and 1 kg P from sewage sludge ash with a complex wet-chemical and heavy metal removal are at a similar level (sludge water: 5.7–6.8 €/kg P; sewage sludge ash: 6.8–7.5 €/kg P). Reason is the significant higher recycling potential from sewage sludge ash. Not considered are distinctly lower costs to recycle P from sludge water at WWTP with higher capacity. In some cases there is no additional economic effort to recovery P from sludge water. With RecoPhos® and using the as in the Fertilizer Industry the additional economic effort of P-recycling (2.1–2.7 €/kg P) can compete with the price of a commercial fertilizer (~2.5 €/kg P).

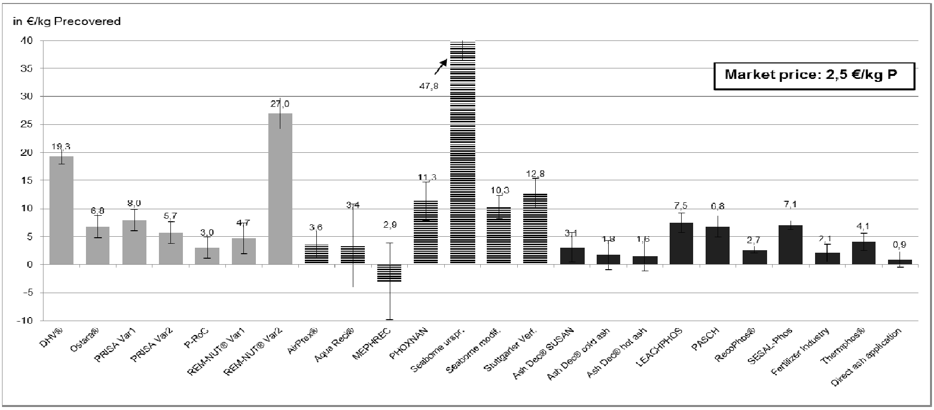


Figure 11: Additional or reduced costs for P-recycling technologies over the whole process chain (€/kg P)

3.4 Final product

Due to the variing potential P sources and technological approaches final products differ strongly with regard to their characteristics. For most of the technologies in sludge water and sewage sludge the precipitation of a non-water soluble salt as magnesium-ammonia-phosphate (MAP) or calcium-phosphate (CaP) is common. With the metallurgic MEPHREC® process a P-rich slag, comparable with the former known ground basic slag is produced. Final products of the wet-chemical process LEACHPHOS, PASCH and SESAL-Phos are CaP with partially relatively high content of aluminum (4–6%). Ash Dec® produces an ash with reduced HM content, while RecoPhos® and the Fertilizer Industry create a product similar to commercial fertilizers.

3.4.1 Plant availability

One of the most import criteria for the final product is the plant availability respectively the actual uptake of a plant of the secondary fertilizers. Often solubility in water, citric acid or other extracting agents is given as an indicator for plant availability, but researches proved this wrong. Mostly data on pot trials (Römer, 2005/2006/2013; Cabeza et al., 2003) as well as field test of the operators themself has been analysed to give an overview about the plant availability. The plant uptake is given for one year and for different soil types (alkaline and acidic soil). In general MAP shows very good plant uptake on acidic soils and partially on alkaline soils over a one year period, although MAP is not soluble in water. Therefore, MAP is comparable with a commercial fertiliser. For CaP the availability is significant lower on both soils, although the different

CaP shows solubility in citric acid comparable to MAP. But the fertiliser effect is merely moderate on acidic soils and in general poor on alkaline soils (DHV Crystalactor®, P-RoC®, AquaReci®, PASCH and SESAL-Phos). For LEACHPHOS® as well a CaP, no data is available so far. Same results can be shown for the decontaminated ash of the Ash Dec® process. With the final product of RecoPhos® (adding phosphorus acid) similar results compared to a commercial fertiliser can be shown. Untreated sewage sludge ash shows a fertilizing effect lower than 25% on acidic soils and lower than 50% on alkaline soils. Generally, further long-term field trials are urgently required to show the actual fertilizing effect of the different secondary fertilizers.

3.4.2 Content of pollutants

As already stated before, the content of pollutant as heavy metals and POPs differs strongly. In order to ensure comparability for those products the method of toxic equivalent model and the self-created reference soil method are applied. The toxic equivalent model is calculated as the coefficient of the heavy metal content of a final product related to a limit value e.g. compost class A. The reference soil method shows the years of application (calculated with an annual load of 40 kg P ha^{-1}) and the limiting heavy metal of the secondary fertiliser on a reference soil with defined heavy metal concentration until a defined tolerated concentration will be exceeded. Sewage sludge, sewage sludge ash and a commercial single superphosphate fertilizer (SSP) are demonstrated as well to enable comparison (Figure 12). For all secondary products a significantly lower toxic equivalent value is demonstrated compared to commercial fertilizer and sewages sludge and –ash. Same results can be shown by the reference soil method, which shows that secondary products can be applied more often (except MEPHREC® and RecoPhos® literature data) until they reach the limiting heavy metal concentration in soil. For the commercial fertilizer Cadmium, a heavy metal with great damage potential, is the limiting metal.

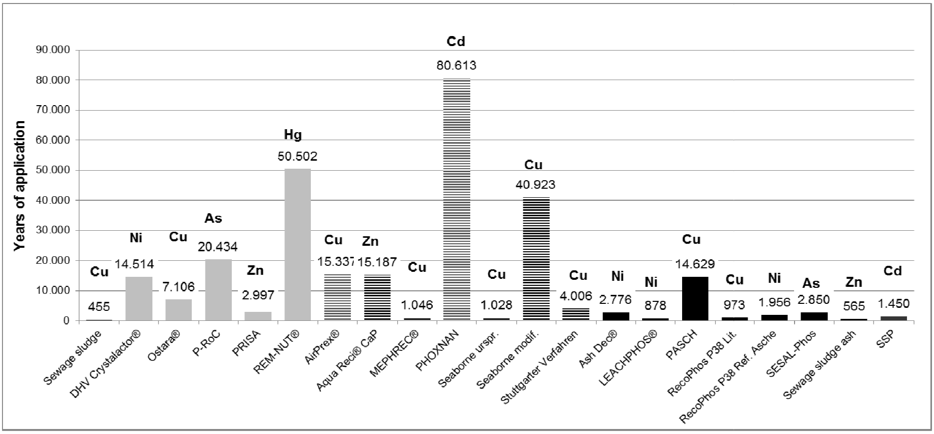


Figure 12: Results of the reference soil method

Advantage of the recycling technologies is as well the removal/destruction of POPs and avoidance of hygienic risks. The products from the sludge water stream show hardly any POPs or pathogenic germs. For the wet-chemical Seaborne® and Stuttgarter Verfahren from sewage sludge, POPs can be detected, but with low concentration. With a wet-oxidative or thermal process, the destruction of POPs and as well pathogen microorganisms can be guaranteed.

3.4.3 Product handling

Requirements to the product characteristics for agriculture application are high. Important criteria's are: storage properties (no dust, no humidity), grain size and strength of the grain for using it in modern application equipment. All produced products can be stored easily, but the criteria for direct application can only fulfilled by Ostara®, DHV Crystalactor® and RecoPhos®. With these processes the required grains/pellets can be produced. For all other products further treatment is necessary (e.g. pelleting).

3.5 Environmental assessment

Quite surprising is the fact that product specific CO_2-emissions (kg CO_2/kg $P_{rec.}$) for recycling technologies from sewage sludge ash are about at the same level or even lower as for technologies from sludge water (5–11 kg CO_2/kg $P_{rec.}$). Same results can be shown for SO_2-emissions (10–50 kg CO_2/kg $P_{rec.}$) and KEA (40–70 kWh/kg $P_{rec.}$). Compared to conventional mineral fertilizer production (-0.5–2 CO_2/kg $P_{rec.}$) and KEA (-

2.4–3 kWh/kg $P_{rec.}$) recycling technologies generally are poor performers, except the two wet-oxidation technologies AquaReci® and PHOXNAN and as well MEPHREC® with the benefit of energy output for P-recycling from sewage sludge. The negative CO_2-emission for the commercial fertilizer is due to use of sulfuric acid, which shows a positive credit due to heat utilization during its production. Hence, technologies with the use of sulfuric acid show better results. Figure 13 shows exemplary the additional/saved CO_2-emissions in case of implementation to the reference situation. Not surprising is the fact, that additional CO_2-emissions for P-recycling technologies from sewage sludge is quite low. Large fluctuations are obvious for the different approaches for P-recycling from sewage sludge. Due to the great resource demand, the emissions of the wet-chemical approaches, RecoPhos® and Thermphos® are significantly higher.

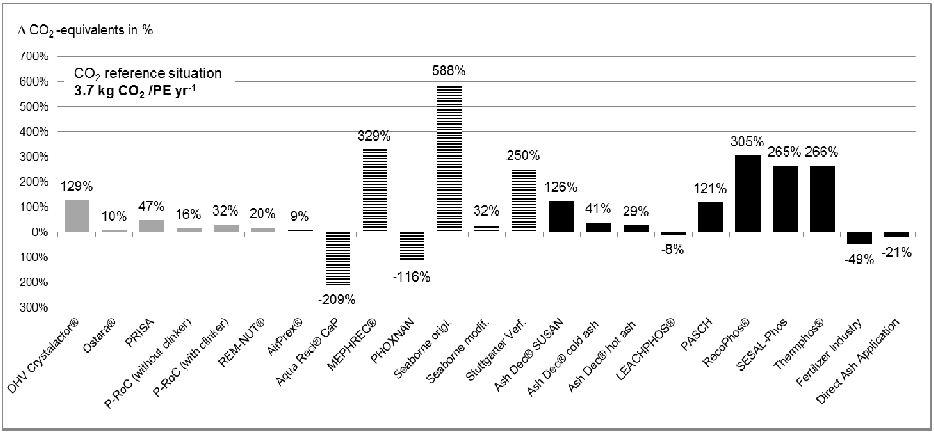


Figure 13: Additional CO_2-emissions (Δ in %) in relation to reference system without P-recycling

4. Summary and Conclusion

With the results of this project, the basis for (political) decision-makers was created to improve the current irresponsible and unsustain use of the P-rich source waste water. By end of 2013 the comprehensive report will be available (http://iwr.tuwien.ac.at/wasser).

Some of the P-recycling technologies, especially the ones applying to sludge water have been implemented already large scale and work successfully. With those technologies secondary fertilizers with the possibility of direct application in agriculture are produced (MAP and/or CaP pellets), showing high purity regarding heavy metals, POPs and hygienic relevant germs and bacteria pollution. Moreover, final products based on MAP show very good plant availability. The resource demand for these technologies is usually limited to e.g. a suitable precipitant and caustic for pH-control. In favorable cases, for waste water treatment plants with a capacity of >200,000 PE, amortization is possible for these technologies by the revenues of selling the secondary product (Ostara® or P-RoC). In Austria, for example only 10 municipal waste water treatment plants have an average capacity of >150,000 PE. Furthermore, requirement for these technologies is a mostly biological phosphorus removal without chemical P-precipitation. In most cases this is not state-of-the-art in Austria. With respect to a great recycling extent of P from waste water these technologies are unsuitable but give operational advantages (avoiding MAP-incrustations or reducing nutrient-back charge).

Technologies which recycle P from sewage sludge use a wide variety of approaches. With the wet-chemical approach (e.g. Stuttgarter and Seaborne® Verfahren) a clean MAP with good plant availability is produced. Nonetheless the recycling quote (<40–50% related to WWTP influent) is low compared to required resource demand. This results in higher annual costs with regard to the recovered phosphorus (9-16 €/kg P), which are significant higher than market prices for commercial mineral fertilizer (2-3 €/kg P). Wet-oxidative approaches as e.g. AquaReci® or PHOXNAN are technically difficult to control and research has been abandoned. Current state of research for metallurgic approaches as e.g. MEPHREC® is still far from developing. Regarding resource demand and costs this approach could be favorable. The path of heavy metals is currently not clarified completely and plant availability for the metallurgic slag seems to be poor on acidic soils. Development potential is given as well as the need for research.

Recycling technologies, which address mono-incinerated sewage sludge ash, have the highest recycling potential (60–90% related to WWTP influent). Furthermore the destruction of pathogenic germs and POPs can be assured to a great extent. Aim of these technologies is the depletion of heavy metals and/or increasing of the plant availability of P. With e.g. the wet-chemical PASCH process a secondary P-product with low heavy metal content is produced but as well with comparative low P-yield (60 70% with respect to WWTP influent). Resource demand is high and therefore additional cost are about 5–10 €/kg P. Technologies as Ash Dec® and RecoPhos® show a higher P-yield, lower resource demand and therefore lower costs (2-6 €/kg P). Plant availability of CaP from wet-chemical technologies and Ash Dec® is limited and unfavorable compared with commercial fertilizers. Besides the technologies with heavy metal removal the aim of RecoPhos® and the Fertilizer Industry (treatment with sulphuric acid) is the improvement of the availability of the chemically bound phosphorus in sewage sludge ash. The additional cost for mono-incineration instead of co-incineration and annual costs for this two approaches is in the range of a commercial P-fertilizer. Nonetheless, no heavy metal removal is intended and therefore total heavy metal load of sewages sludge ash remains in the final fertilizer and is applied together with other P-containing fertilizers in agriculture.

Overall the technologies to recover phosphorus from sewage sludge ash show ideal prerequisites to recycle phosphorus to a large extent. However, mixing of sewage sludge with combustibles poor in phosphorus must be avoided (mono-incineration). Further advantage of an appropriate strategy is that there is no bond to the location of a waste water treatment plant and the implementation of large central units is possible. Furthermore, this option offers the possibility of combined combustion and recycling from other P-rich sources as meat and bone meal. The decision, on which of the technologies the preference is given, depends on the requirement to the characteristics of the final product and plant availability. Whereas technologies without or with low removal of heavy metals produce already a plant available product with costs compared to a commercial P-fertilizer. Otherwise the technologies with the aim of a very clean product are not implemented large scale so far, products are not competitive to commercial fertilizers with regard to the plant availability and the costs are clearly higher. Purely economic aspects are currently not the driving force for the implementation for one of these technologies. Thus, additional incentives or particular legal constraints are necessary.

Literature

Binder, C., De Baan, L., Wittmer, D. (2009) Phosphorflüsse in der Schweiz. Stand, Risiken und Handlungsoptionen. Final Report. Umwelt-Wissen Nr. 0928. Bundesamt für Umwelt, Bern; 2009.

Brunner, P., Rechberger, H. (2004) Practical handbook of material flow analysis. Boca Raton, FL: CRC/Lewis. 2004.

Cabeza, R., Steingrobe, B., Römer, W., Claassen, N. (2011) Effectiveness of recycled P products as P fertilizers, as evaluated in pot experiments. Nutrient Cycling in Agroecosystems 91 (1), pp. 173-184.

Cordell D, Drangert J O, White S. The story of phosphorus: Global food security and food for thought. Global Environment Change 19 (2), pp. 292-305.

Cencic, O., Rechberger, H. (2008) Material Flow Analysis with Software STAN. Journal of Environmental Engineering and Management (JEEM) 18 (1), pp. 3-7.

Egle, L., Zoboli, O., Thaler, S., Rechberger, H., Zessner, M. (2013) The Austrian P-budget as a basis for resource optimization. Resources, Conservation & Recycling, Accepted and in Press.

GEMIS (2013) GEMIS - Globales Emissions-Modell Integrierter Systeme. Öko-Institut (Institut für angewandte Ökologie e.V.). Darmstadt.

Gethke-Albinus, K. (2012) Verfahren zur Gewinnung von Sekundärphosphaten aus flüssigen Stoffströmen und deren Einfluss auf die deutsche Phosphorbilanz [Dissertation]. Aachen (Germany): Technical University of Aachen – Faculty of Civil Engineering; 2012.

Montag, D. (2008) Phosphorrückgewinnung bei der Abwasserreinigung - Entwicklung eines Verfahrens zur Integration in kommunalen Kläranlagen. Dissertation an der Fakultät für Bauingenieurwesen der Rheinischen-Westfälischen Technischen Hochschule Aachen.

Römer, W. (2005) Vergleichende Untersuchung der Phosphatverfügbarkeit von Produkten des P-Recyclings und bekannter Phosphatdünger. Korrespondenz Abwasser, Abfall. (53) Nr. 5, pp. 483-489.

Römer, W. (2006) Vergleichende Untersuchungen zur Pflanzenverfügbarkeit von Phosphat aus verschiedenen P-Recycling-Produkten im Keimpflanzenversuch. Journal of Plant Nutrition and Soil Science. Vol. 169, pp.826-832.

Römer, W. (2013) Phosphor-Düngewirkung von P-Recyclingprodukten. Korrespondenz Abwasser, Abfall. Vol. 60 (3), pp. 202-215.

Authors

Lukas Egle, Helmut Rechberger, Matthias Zessner

Vienna University of Technology

Karlsplatz 13/226-1

1040 Vienna, Austria

0043 1 58801 22633

Phosphate recycling in mineral fertilizer production

C.P. Langeveld and K.W. ten Wolde

ICL Fertilizer, Amsterdam

Summary

Phosphate recycling is an important issue, since it is a finite resource which is essential to food security. The phosphate used in the fertilizer industry, which now solely comes from mining, has to be replaced with so-called secondary phosphates. Different sources present opportunities to recover phosphates, the most important being manure, litter, wood ashes, sewage sludge ashes, meat- and bone meal ashes and struvite.

At ICL Fertilizers, trials have been conducted to investigate the potential implementation of these sources of secondary phosphates into the fertilizer production. Extensive pilot-scale testing and several plant-scale tests have yielded promising results for the use of sewage sludge ash, meat- and bone meal ash and struvite. These sources are readily available for implementation and require only little modifications to the current fertilizer production facilities of ICL. Also, the environmental impact of producing fertilizer using these secondary phosphate sources suggests the emissions of phosphate and fluorine is lower than with regular phosphate rock.

The main issue remaining is the legislation for the use of these sources, as they are currently regarded as waste. Struvite is also suspected to be able to contain contaminants such as pathogens and pharmaceuticals, encapsulated in its crystals. Therefore, further research on this topic is necessary. In the WG3 meetings of the European Commission, maximum values for heavy metal content in fertilizer were specified in greater detail. The first results show that products produced from sewage sludge ash meets these demands. Since heavy metal content in struvite and meat- and bone meal ash is low, no problems are expected.

The use of secondary phosphate in fertilizer production yields great opportunities.

Keywords: secondary phosphate, struvite, sewage sludge ash, meat- and bone meal ash, acidulation, granulation

1. Introduction

For some other finite resources, like oil, it is possible to find alternative sources. For phosphorus this is not the case as this is a chemical element (Heffer, Prud'homme, Muirheid, & Isherwood, 2006). Therefore, usage has to be cut to make the reserves last longer. Still, this will not make phosphorus an infinite resource (Van Vuuren, Bouwman, & Beusen, 2010). Closing the phosphorus cycle by recovering and recycling will be required if phosphorus famine is to be prevented (Gilbert, 2009).

Phosphorus is disposed of in human excreta, used detergents and food- and industrial waste. This stream enters the sewage systems and offers an opportunity to recover it as it accumulates in the sewage sludge at waste water treatment plants. The sewage sludge can be processed in many different ways to recover the phosphorus (Schick, Kratz, Adam, & Schnug, 2009). These can be summarized into three main categories, the watery sludge, dewatered sludge and sewage sludge ash. At waste water treatment plants, struvite, which is essentially magnesium ammonium phosphate, can also be formed by crystallisation and precipitation. This feedstock also contains a high level of phosphorus and can be regarded as a secondary phosphate source (Jaffer, Clark, Pearce, & Parsons, 2002).

Next to the wastewater treatment plants other sources exist (Schipper et al., 2001). Since the ban on the use of meat- and bone meal as animal feed due to the outbreak of BSE, it is classified as a waste material (Yamamoto et al., 2006). The meat- and bone meal is incinerated, rendering it harmless but this also renders it useless for its traditional uses. The phosphate content in this is even higher than sewage sludge ash and it contains less contaminants.

The nutrient availability for plants of the phosphate is imperative for it to be used in a fertilizer (Cabeza, Steingrobe, Römer, & Claassen, 2011). The solubility in neutral ammonium citrate and water, which with phosphate rock is realised by acidulating, is important. The processing for this will be discussed in chapter 4.

The main issue regarding the use of secondary phosphates is legislation, as the streams currently being tested are regarded as waste. Also, some contaminants are present in selected sources. In sewage sludge ash for example, a relatively high amount of heavy metals are present. This does not, however, have to be an issue.

1.1 ICL Fertilizers' position

ICL Fertilizers runs several fertilizer production units in different parts of the world. All of them are based on the attack of phosphate rock with sulphuric acid, phosphoric acid, or combinations of the two (secondary attack) after which potassium chloride (MOP) or potassium sulphate (SOP) or trace elements (Cu, Mg,Mn, Mo, Zn, etc) can be added to make different forms of PK's and on top of that ammonium sulphate to produce NPK's. These processes are very suitable for the recycling of secondary phosphates (contrary to other NPK processes) without any safety issue.

Figure 1.1: ICL Fertilizers' production plant in Amsterdam

At ICL Fertilizers in Amsterdam a lot of research and testing has been done regarding the use of secondary phosphates in the fertilizer production. Extensive pilot-plant scale tests (Ten Wolde, 2012) have been done regarding the use of struvite as well as that of sewage sludge ash en meat- and bone meal ash. Acidulation of sewage sludge ash and addition of struvite to fertilizer have also been carried out on plant-scale tests.

As a phosphate fertilizer producer with an own supply of phosphate in the Israeli desert, it could be perceived as odd to be researching the use of secondary phosphates. The vision of ICL Fertilizers is that sustainability is important and the environment is to be taken care of. ‘Closing the loop’ on phosphorus could elongate the use of the phosphate mines and improve the distribution of phosphorus on a world-wide scale. The fact that ICL’s European plants are in countries with excess phosphate, adds to this philosophy: using a part of all recycled phosphate in plants that export a major part of their products to countries with a deficit on phosphate, help solving the existing surplus in The Netherlands and Germany.

1.2 Value chain agreement

In The Netherlands, ICL Fertilizers Europe has taken part in the so-called value chain agreement, initiated by The Nutrient Platform in 2011. Together with nineteen other parties the ambition is to create a sustainable market where reusable phosphate streams will be returned to the cycle in an environmental-friendly way. ICL Fertilizers Europe’s ambition is to base its entire fertilizer production on secondary phosphates by 2025. By 2015, a figure of 15% will be attainable (Dutch Nutrient Platform, 2011).

Since the Netherlands has a surplus of phosphate, the expansion to a European Union based platform was desirable. In 2013, at the European Sustainable Phosphate Conference in Brussels, the European Phosphorus Platform was launched, with over 150 participants. This is an important development to move forward and could improve Europe’s competitive position and avoid potential geopolitical tensions (European Phosphorus Platform, 2013).

2. Secondary phosphate sources

Different sources are available within the European Union. These can be categorized in three main categories. These are manure and litter, phosphate-rich ashes and struvite.

The main differences between these sources are the solubility of phosphate and the contaminants it can contain. Also the physical form is an important factor that differs. These facts impact the way the secondary phosphates can be employed in the produced fertilizers. In this chapter, the properties of the sources will be discussed.

2.1 Manure and litter

Several countries, such as the Netherlands, with intensive livestock agriculture have a surplus of animal manure and poultry litter. Since these contain phosphates, research is being done to be able to use these as a raw material for fertilizer production.

Untreated manure contains organic components and water and are of a low nutrient content. For industrial applications it therefore needs to be dewatered and incinerated (Schipper et al., 2001). These ashes could be employed as raw material for the fertilizer production in secondary attack units in the same way as sewage sludge ashes.

Other techniques currently being researched is the pyrolysis of manure (Azuara, Kersten, & Kootstra, 2013) and the gasification of chicken litter (Kaikake, Sekito, & Dote, 2009). The products from these processes could also be implemented in the production of phosphate fertilizer.

2.2 Ashes from mono-incineration

The phosphate-rich ashes are a product of mono-incineration of a phosphate-rich stream, such as from wastewater treatment plants or meat- and bone meal from rendering factories. Due to the incineration of phosphate-rich streams separately from phosphate-poor streams, relatively high phosphorus content can be achieved in the ash.

2.2.1 Sewage Sludge Ash

At wastewater treatment plants, contaminants are precipitated using iron- or aluminium compounds. Here sewage sludge accumulates. This sludge contains a number of nutrients that can be recycled, such as phosphate. The substitution potential of recovered phosphorus from sewage sludge in Germany is estimated at 40% (Schaum, Cornel, & Jardin, n.d.). There are a lot of differences in the EU regarding sewage sludge; in The Netherlands, 100% is incinerated while in Spain almost all sewage sludge is used agriculturally as reported by Eurostat in 2009. Even within countries such as Germany, differences can be significant: in the northern part, 60% is used in agriculture whereas this is only 20% in the southern part.

Recovery can be done directly from the sludge, from dewatered sludge or incinerated sewage sludge ash. Wet or dewatered sludge is not suitable for the traditional industrial processing, as these streams contain water and could contain organic compounds, viruses, medicine and other contaminants. These can be rendered harmless by incinerating the sludge.

This yields sewage sludge ash. Dewatered sewage sludge is incinerated in dedicated furnaces as not to introduce more contaminants from other streams such as industrial waste, further diluting the phosphate content (European Commission, 2000). As this is the form from which over 90% can be recovered, this is the most interesting and it could be possible to integrate it into existing infrastructure (Cornel & Schaum, 2009).

Another advantage of incineration of the sewage sludge is that it has a caloric value, so it yields energy on incineration.

Currently, a fair amount of sewage sludge ash is disposed to landfill. This is being limited by the EU Landfill Directive, which in turn will increase the availability of sewage sludge ash for the use in fertilizer production.

The main problem with sewage sludge ash (SSA) is the content of heavy metals, iron and aluminium. These hinder the regular processing, which will be discussed in chapter 3. Since the flocculants for sewage sludge vary, several different analyses are shown in table 2.1 and 2.2. A sewage sludge ash sample is depicted in figure 2.1.

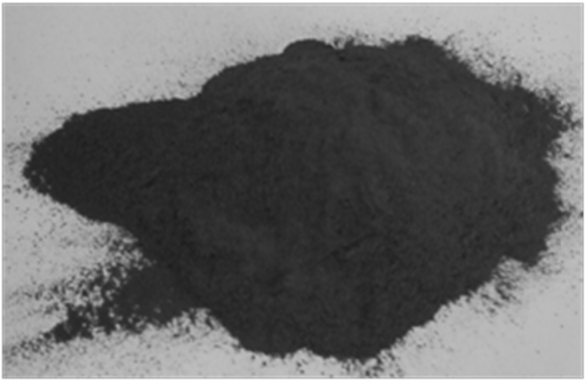


Figure 2.1: Sewage sludge ash

Table 2.1: Analyses of the main components of sewage sludge ash (SSA), meat and bone- meal ash (MBMA) and phosphate rock

Total wt%	SSA 1	SSA 2	SSA 3	SSA 4	MBMA	Wood ash	Phosphate rock
P_2O_5	15,20	20,44	18,90	17,80	25,50	4,8	30,96
CaO	18,80	20,59	11,50	18,60	37,40	13,5	47,50
SO_4	5,30	4,50	1,60	3,00	6,40	6,2	2,70
K_2O	1,30	1,66	0,80	1,20	2,20	14,8	0,70
MgO	2,30	2,74	1,19	2,90	0,99	8,1	0,40
Al_2O_3	6,28	9,39	9,44	9,20	1,74	12,9	0,11
Fe_2O_3	12,08	5,82	3,05	5,60	0,99	9,5	0,17

Table 2.2: Heavy metal content analyses of sewage sludge ash (SSA), meat- and bone meal ash (MBMA) and phosphate rock

ppm	SSA 1	SSA 2	SSA 3	SSA 4	MBMA	Wood ash	Phosphate rock
As	20,1	19,9	9,4	9,0	8,1	0,4	17,8
Cd	2,1	1,0	2,2	<0,1	1,7	<0,2	25,9
Cr	115,5	124,5	25,0	79,5	18,1	1,0	53,0
Cu	760,3	1146,0	404,0	749,6	365,0	1,5	13,5
Ni	44,6	49,6	17,8	37,7	7,8	1,1	30,7
Mn	871,6	825,5	3070,0	719,4	207,0	11,7	6,7
Pb	273,0	254,0	157,6	84,4	82,4	2,2	< 0,1
Zn	3053,0	2139,0	876,0	1624,0	209,0	-	260,2

2.2.2 Meat- and bone meal ash

Prior to 2001, meat- and bone meal (MBM) was primarily used in animal feed, but in 2001 this was banned in Europe due to the fact that MBM was suspected to be the cause of the mad cow decease outbreak (Yamamoto et al., 2006). This caused large-scale waste problems which were solved by incinerating the MBM and thus creating meat- and bone meal ash (MBMA) (Cascarosa, Gea, & Arauzo, 2012).

This meat- and bone meal ash is very similar to regular phosphate rock in terms of chemical composition. Also the content of contaminants is very low, as can be seen in table 2.1 and 2.2. The product received at ICL fertilizers for testing can be seen in figure 2.2.

Figure 2.2: Meat- and bone meal ash

2.2.3 Wood ashes

Several initiatives are taking place to incinerate clean waste wood as a bio-fuel. The ashes coming from this incineration are fairly pure and contain phosphates and potash as valuable nutrient, however in a not-available form for plants. They can however be transformed by secondary attack into soluble fertilizers. For analysis results, see table 2.1 and 2.2

2.3 Struvite

At wastewater treatment plants, struvite crystallization is a widely used technique to remove phosphorus, ammonium from digested sludge liquors (Martí, Pastor, Bouzas, Ferrer, & Seco, 2010) by adding a source of soluble Mg in the proper stoichiometric ratio. Struvite is sometimes also referred to as MAP (Magnesium Ammonium Phosphate) and consists of these ions in a molar ratio of 1:1:1. The reaction that takes place is shown in equation (2.1).

$$Mg^{2+} + NH_4^{+} + PO_4^{3+} + 6\,H_2O \rightarrow MgNH_4PO_4.6H_2O \qquad (2.1)$$

The spontaneous formation of struvite can cause scaling in piping and equipment at wastewater treatment plants and the controlled removal of the building blocks is thus also beneficial for these plants (Jaffer et al., 2002). Analysis of struvite has also shown a very low content of heavy metals, which is beneficial with regard to the possible use in fertilizer.

Since struvite is not incinerated, a certain fear exists that it could contain pathogens, pharmaceuticals, hormones and other contaminants encapsulated in the crystals (Decrey, Udert, Tilley, Pecson, & Kohn, 2011; Ronteltap, Maurer, & Gujer, 2007). Research on struvite precipitated from urine has shown that 98% of the hormones and pharmaceuticals remained in the filtrate and only a small fraction of the heavy metals remained in the struvite. Drying has shown to be effective to inactivate viruses that could be present in the struvite. Heating struvite to a temperature higher than 40 to 55°C causes it to decompose, releasing gaseous ammonia (Bhuiyan, Mavinic, & Koch, 2008). Therefore, drying should be done in a controlled fashion and further research is needed in this field.

Struvite can be obtained from several different processes. Analyses from these struvite are shown in table 2.3 and 2.4, with a phosphate rock analysis for comparison.

The Airprex process was developed by the Berlin Wasserbetriebe in 2007 in order to reduce the problems with spontaneous struvite precipitation. By aerating the digested sludge, CO_2 is stripped which increases pH while simultaneously magnesium is added to the system to promote crystallisation. The crystals will then settle at the bottom and are removed through the outlet. A schematic presentation of the position in a waste water treatment plant and the setup is shown in figure 2.3. The washed struvite crystals are shown in figure 2.4.

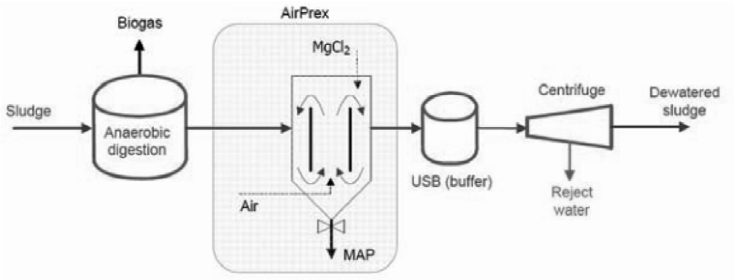


Figure 2.3: Schematic of the Airprex process' position in a WWTP (STOWA, 2012)

Figure 2.4: Struvite crystals from the Airprex process (STOWA, 2012)

The Anphos process is very similar to the Airprex process, as it also involves a pH-shift by aerating and magnesium dosing. The struvite from the Anphos process received at ICL Fertilizers was crystallised from the washing water of a potato processing facility. A photograph of the struvite is shown in figure 2.5.

Figure 2.5: Struvite from the Anphos process as received in bulk

Table 2.3: Analyses of the main components of Airprex and Anphos struvite and phosphate rock

wt% (TQL)	Struvite Airprex	Struvite Anphos	Phosphate rock
Total P_2O_5	19,8	14,7	30,96
NH_4	3,8	2,6	0,00
CaO	0,8	2,3	47,50
SO_4	0,1	0,5	2,70
MgO	10,2	7,6	0,40
Al_2O_3	0,1	< 0,1	0,11
Fe_2O_3	1,5	0,3	0,17
Moisture	14,9	21,9	1,8

Table 2.4: Analyses of the heavy metal content of Airprex and Anphos struvite and phosphate rock

ppm	Struvite Airprex	Struvite Anphos	Phosphate rock
As	< 0,1	0,0	17,8
Cd	< 0,1	0,0	25,9
Cr	11,1	0,0	53,0
Cu	31,6	2,0	13,5
Hg	< 0,1	0,0	< 0,1
Ni	3,6	0,0	30,7
Mn	< 0,1	12,0	6,7
Pb	652	0,0	0,0
Zn	85,9	11,0	260,2

3. Processing in mineral phosphate fertilizer production

The main two types of secondary phosphates which can be used in the production of phosphate fertilizer are ashes from mono-incineration such as meat- and bone meal ash, wood ash, sewage sludge ash and struvite. At ICL fertilizers, these have been extensively tested on a pilot scale and some have also been tested on plant-scale in Amsterdam. The results of these tests will be discussed in this chapter, as well as the technical implications it has on the current infrastructure at the production location in Amsterdam. Since the plant in Ludwigshafen, Germany is quite similar to that in Amsterdam, the implementation can also be done here.

3.1 Ashes from mono-incineration

As well in sewage sludge ash as in wood and meat- and bone meal ash, the phosphate is not soluble in water or neutral ammonium citrate and thus not plant available. With phosphate rock, acidulating the rock with either sulphuric- or phosphoric acid will yield single or triple superphosphate respectively. These fertilizers have a typical water and NAC solubility of 90-92% and 95-97%. The reaction equations of the acidulation to single- and triple superphosphate are shown in equations (3.1) and (3.2) (Kongshaug et al., 2000).

$$2\ Ca_5(PO_4)_3.F + 7\ H_2SO_4 \leftrightarrow 3\ Ca(H_2PO_4)_2 + 7\ CaSO_4 + 2\ HF \quad (3.1)$$

$$2\ Ca_5(PO_4)_3.F + 7\ H_3PO_4 \leftrightarrow 5\ Ca(H_2PO_4)_2 + 2\ HF \quad (3.2)$$

Phosphate from ashes is not present in the form of apatite ($Ca_5(PO_4)_3(F,Cl,OH)$), but in complexes with iron, calcium or aluminium. Due to this different form and the presence of other contaminants such as heavy metals which could react with the acid, a regular acidulation mixture does not yield the physical and chemical results required. Another important difference between the apatite and these ashes is that the apatite contains fluorides, chlorides, hydroxides and carbonates. During acidulation, these are released into gaseous form such as HF, HCl and CO_2. In order to create sufficient surface area during the acidulation process, which delivers a product that is softer and better processable, some additives have to be mixed with the ash prior to acidulation.

These ashes are much finer than regular phosphate rock. Therefore, milling is not necessary. This does impact the handling and storage. Therefore, storage in silos and direct input in the mixers is desirable.

3.1.1 Meat- and bone meal ash

Meat- and bone meal ash shows most similarities with apatite; the phosphate is mainly present as calciumphosphate. This reacts with acid in a similar way as apatite, as can be seen by comparing equations 3.1 and 3.2 with 3.3 and 3.4.

$$Ca_3(PO_4)_2 + 3\ H_2SO_4 \leftrightarrow 3\ Ca(SO_4) + 2\ H_3PO_4 \quad (3.3)$$

$$Ca_3(PO_4)_2 + 4\ H_3PO_4 \leftrightarrow 3\ Ca(H_2PO_4)_2 \quad (3.4)$$

This suggests that regular acidulation with a slightly different acid concentration would be possible. Also, since the meat- and bone meal ashes have a phosphate content that almost reaches the concentration found in phosphate rock, it can be mixed with phosphate rock to achieve regular products. During extensive tests on pilot-scale at ICL Fertilizers, it has shown that this is the case. Mixing with regular phosphate rock was possible, achieving a high water solubility and neutral ammonium citrate solubility yield. The physical properties of the produced superphosphate are also similar to that of phosphate rock.

Besides a mixed acidulation with phosphate rock, acidulation of pure MBMA was also possible and yielded good results with regards to the chemical properties. The physical properties of the acidulated MBMA did impact the processability and at this moment a mixture with phosphate rock is preferred.

3.1.2 Sewage sludge ash

As shown in table 2.1 and 2.2, the levels of aluminium, iron and heavy metals are much higher than that in phosphate rock or meat- and bone meal ash. Next to the fact that it is possible for the phosphate to be present in complexes with the iron- and aluminium, it is also possible for the acid to react with these.

As can be derived from Gibbs free energy calculations (Dean, 1979; Langeveld & ten Wolde, 2013; Lide, 2008), the formation of iron phosphate and superphosphate are highly favoured thermodynamically in standard conditions. As phosphoric acid is formed during the acidulation of the sewage sludge ash, the available iron oxide is suspect to form iron phosphate which results in less free phosphoric acid to react to superphosphate.

Acidulation

Acidulation of different sewage sludge ashes has been tested at ICL Fertilizers. This resulted in a large spread in the resulting products.

Since the contaminant levels are high in the sewage sludge ash, mixtures with phosphate rock showed only negative effect. Acidulation using phosphoric acid also did not yield good results, as the product did not coagulate fully, which was not processable. Therefore, only acidulation using sulphuric acid was further tested.

Three sewage sludge ashes with a different iron-content were acidulated and monitored in time, since the water solubility in acidulated phosphate rock increases in time as the reaction continues. This increase in time was not noticed with the sewage sludge ashes. The water solubility of the reaction product is a clear function of the iron and aluminium content of the ash. The solubility in neutral ammonium citrate of these products shows the same dependency, be it that in general Al-based ashes are reducing recoveries less that Fe-based ashes.

Another important factor for employing sewage sludge ash in the production of phosphate fertilizer is its physical properties. Regular acidulation mixtures showed a sticky product, which was not processable. Removing part of the water and thus increasing the acid concentration showed positive effect on this. The iron-based sewage sludge ashes delivered less processable products, regardless of the used acid concentration.

The acidulation has also been tested at ICL Fertilizers on plant-scale, which resulted in good acidulation of 10 to 14 tons sewage sludge ash (7wt% Fe_2O_3) per hour. No optimised acidulation mixture has been found yet for the acidulation on plant-scale, since tests need to be continued. The resulting product did show good physical and chemical properties.

Granulation

To check the granulation properties, several different recipes were used. Six PK- and four P-fertilizer granulations were executed in the initial trials. The conclusion found from these results is that the optimum for using sewage sludge ashes is making a specific mixture of acidulated high reactive Israeli rock phosphate with acidulated sewage sludge ash in the granulator. This caused the granulation to yield a good granule size distribution and a proper nutrient content.

During the granulation, the temperature was over 10°C higher than regular phosphate rock granulation. In the PK granulation, this could be attributed to the exothermic reaction taking place between the free acid and potash as shown in equation (3.5). During granulation some hydrochloric acid fumes were noticeable. However, this temperature rise is also present in the P-only fertilizer, of which the temperature rise cannot be ascribed to this reaction (Schultz, Bauer, Schachl, Hagedorn, & Schmittinger, 2000). In the used setup, it was impossible to determine the cause of this.

$$KCl + H_2SO_4 \rightarrow KHSO_4 + HCl \quad (3.5)$$

Besides this difference in temperature, the granulation process itself is more sensitive. More water is needed for the granulation to start and the granulation is more prone to spontaneous over-granulation than is the case with comparable non-SSA containing fertilizers.

When granulating the mixtures, the P_2O_5 water soluble yield was not proportional to the yield in both components. This suggests there could be a reaction taking place during granulation, which could also attribute to the temperature increase.

At the moment of this writing, no plant-scale granulation test has been carried out yet where a significant amount of acidulated sewage sludge ash was employed.

3.2 Struvite

Unlike the ashes from mono-incineration, the phosphate in struvite is readily neutral ammonium citrate soluble. Therefore, the acidulation step does not have to be carried out on this feedstock which simplifies the processing of it.

Several plant-scale tests have been carried out with struvite as a secondary phosphate. Struvite obtained by the Airprex-process from a wastewater treatment plant was very well usable and could be added to a maximum of 20% of the total granulation input. The moisture content of the used struvite appeared to be the limiting factor. As the struvite used in the plant-scale test contained between 15% and 20% moisture, water and steam addition to the granulation drum had to be limited and smearing occurred on several points.

The main differences in the obtained products using struvite are a decrease in heavy metal content and water soluble phosphate and an increase in pH. Emission measurements for fluorine, phosphorus and chloride were also performed during the granulation of a PK 8-27+7MgO, which indicated lower emissions when struvite was added. Phosphate and fluorine emissions to wastewater decreased, indicating a positive impact on the environment.

4. Future perspective

There are several different processes in development, based on different principles such as leaching and thermic treatment. These will not be discussed in this report.

4.1 Implementation at ICL Fertilizers

At the moment of this writing, an investment proposal is being prepared at ICL Fertilizers in Amsterdam in order to store and process sewage sludge- and meat- and bone meal ashes. The ambition is to use 25-30 kilotons of sewage sludge ash by 2015. If the process proves itself, a significant increase in the use of sewage sludge ash in Germany can be achieved by implementing this at ICL's Ludwigshafen plant.

This will entail several silos with dosing units and transportation systems directly into the mixers for acidulation. An important ability is to achieve a constant flow in the necessary composition of the components. It should also be possible to mix milled phosphate rock from the regular process with e.g. meat- and bone meal ash from this system at the mixer input. The pre-engineering led to a proposal for three silos with gravimetrical dosing and pneumatic transportation to the mixers. This way, a flow of 15 ton per hour can be achieved to each of the mixers.

5. Challenges and issues

5.1 Legislation

As sewage sludge ash, struvite and meat- and bone meal ash are currently regarded as waste, at this moment they cannot be employed as feedstock in commercial fertilizer. It is imperative that these streams will not be regarded as waste in the future, thus making nutrient recovery from these streams more practicable.

MBMA processing does not pose any threat to the environment and ecology, but even reduces emissions because of the lack of fluoride and other gas forming substances. When regarding the processing of SSA, the emissions are also lowered due to the absence of gas forming substances. During a plant-scale test with struvite addition to the granulation, the emissions of fluorine and phosphate showed lower figures than without struvite in PK production. However another trial with struvite had to be stopped due to smell issues from co-crystallized organic material. It proves each material source needs careful checking before processing.

With regards to struvite, further research is needed to prove that no pathogens, pharmaceuticals or other hazardous contaminants remain present; it is imperative that no risks are carried over to the fertilizer. Research on the Airprex-derived struvite employed during tests at ICL Fertilizers is being executed by an external laboratory for possible risks. Several Dutch waterboards are currently also working on a joint research with 'Stichting Toegepast Onderzoek Waterbeheer' in order to research the contaminants present. At the moment of this writing, no further information was available regarding this issue.

The cadmium content for both MBMA and SSA are far lower than that of phosphate rock. This results in lower cadmium levels in the final products. The SSA however, does contain heavy metals that are not present in the phosphate rock. The acidulated sewage sludge ash was compared to the EU's guidelines for heavy metal content as setup during the WG3 meetings on 20 September 2012; the maximum values are shown in table 5.1 (Berend & Severin, 2012). Comparing the heavy metal content in acidulated sewage sludge ash with these numbers, it can be seen that this does not exceed the set limits. Also, when a mixture of acidulated phosphate rock and sewage sludge ash is granulated, the values, except for cadmium, will be even lower.

Table 5.1: WG3 limits for heavy metals in fertilizer compared to acidulated sewage sludge ash

ppm	As	Cd	Cr	Hg	Ni	Pb
Acidulated SSA	6,8	2,6	74,0	0,0	30,7	84,0
Limit WG3	60,00	3,00	100,00	2,00	90,00	140,00

6. Conclusions

The use of secondary phosphates in the mineral fertilizer industry yield great opportunities. Many different sources are possible, which could guarantee security of supply and keep the market healthy with regards to competition. This also contributes to a healthy phosphate balance, since this way countries with a surplus of phosphate could remove it from the cycle and export it through fertilizer to countries which have a phosphate deficiency.

Technically, it is already possible to replace a great deal of phosphate rock with secondary phosphates from struvite and mono-incineration ashes. However, legislation and safety issues still exist. The classification of these products as 'waste' obstructs their current employment on an industrial scale. It is imperative that the legislation issues are addressed as quickly as possible and it should get the full attention at the European Committee. The launch of the European Phosphorus Platform emphasises this and could contribute to these issues.

Regarding struvite, it is important that further research is done on the contaminants it could contain. Following this, the struvite could then easily be used in the production of phosphate fertilizer as the phosphate it contains is already soluble and thus plant-available. The processability of struvite does vary, as the odour emissions and moisture content varies. These are issues that should be kept in mind and every struvite source is therefore to be tested and reviewed individually.

As sewage sludge ashes have a high content of heavy metals, this could become an issue with regards to accumulation in the soil where the fertilizer is applied. The products from sewage sludge ash do meet the set limits from the European Commission's WG3 meetings, but with further research and development it could be possible to reduce the emissions of the heavy metals to the environment even more. As was seen in trial experiments, sewage sludge ashes with a high content of iron did not acidulate as well as the ashes with a lower concentration of iron. If the sewage sludge streams and applied flocculants could be managed in a better fashion, it could be possible to achieve even better results regarding phosphate recovery from sewage sludge ashes.

Meat- and bone meal ashes are the best applicable at the moment, as these show most similarities with regular phosphate rock. Therefore, no real issues exist with the implementation of this feedstock into the production of mineral phosphate fertilizer.

Other sources, such as manure, litter and wood ashes also pose interesting sources. Technology is still being developed to optimise the recovery of phosphate from these sources, such as pyrolysis of manure and wood ash. If the phosphate content is high enough in a certain stream, it could become an interesting source to look into.

With the new technologies in development such as the leaching processes and thermochemical treatment of P-rich streams such as sewage sludge ash, cleaner and better usable phosphorus streams are expected to emerge in the future. This will deliver even better results for fertilizer production, further closing the phosphorus cycle and making the fertilizer industry more sustainable.

References

Azuara, M., Kersten, S. R. A., & Kootstra, A. M. J. (2013). Recycling phosphorus by fast pyrolysis of pig manure: Concentration and extraction of phosphorus combined with formation of value-added pyrolysis products. Biomass and Bioenergy, 49, 171–180. doi:10.1016/j.biombioe.2012.12.010

Berend, K., & Severin, K. (2012). Working Group 3 – Contaminants, hygene and other risks (pp. 1–14). Brussels.

Bhuiyan, M. I. H., Mavinic, D. S., & Koch, F. A. (2008). Thermal decomposition of struvite and its phase transition. Chemosphere, 70(8), 1347–56. doi:10.1016/j.chemosphere.2007.09.056

Cabeza, R., Steingrobe, B., Römer, W., & Claassen, N. (2011). Effectiveness of recycled P products as P fertilizers, as evaluated in pot experiments. Nutrient Cycling in Agroecosystems, 91(2), 173–184. doi:10.1007/s10705-011-9454-0

Cascarosa, E., Gea, G., & Arauzo, J. (2012). Thermochemical processing of meat and bone meal: A review. Renewable and Sustainable Energy Reviews, 16(1), 942–957. doi:10.1016/j.rser.2011.09.015

Cornel, P., & Schaum, C. (2009). Phosphorus recovery from wastewater: needs, technologies and costs. Water science and technology : a journal of the International Association on Water Pollution Research, 59(6), 1069–76. doi:10.2166/wst.2009.045

Dean, J. A. (1979). Lange's Handbook of Chemistry. Lange's Handbook of Chemistry (12th ed.). McGraw-Hill.

Decrey, L., Udert, K. M., Tilley, E., Pecson, B. M., & Kohn, T. (2011). Fate of the pathogen indicators phage ΦX174 and Ascaris suum eggs during the production of struvite fertilizer from source-separated urine. Water research, 45(16), 4960–72. doi:10.1016/j.watres.2011.06.042

Dutch Nutrient Platform. (2011). Phosphate Value Chain Agreement. The Nutrient Platform.

European Commission. (2000). Disposal and recycling routes for sewage sludge, (October 1999).

European Phosphorus Platform. (2013). Press Release ESPC13. Brussels: The Nutrient Platform.

Gilbert, N. (2009). The disappearing nutrient. Nature, 461(October), 716–718. doi:10.1016/j.amjmed.2010.04.007

Heffer, P., Prud'homme, M. P. R., Muirheid, B., & Isherwood, K. F. (2006). Phosphorus fertilisation: Issues and outlook. In Proceedings International Fertiliser Society. York: 586.

Jaffer, Y., Clark, T. A., Pearce, P., & Parsons, S. A. (2002). Potential phosphorus recovery by struvite formation, 36, 1834–1842.

Kaikake, K., Sekito, T., & Dote, Y. (2009). Phosphate recovery from phosphorus-rich solution obtained from chicken manure incineration ash. Waste management (New York, N.Y.), 29(3), 1084–8. doi:10.1016/j.wasman.2008.09.008

Kongshaug, G., Brentnall, B. A., Chaney, K., Gregersen, J.-H., Stokka, P., Persson, B., … Skauli, Ø. (2000). Phosphate Fertilizers. In Ullmann's Encyclopedia of Industrial Chemistry. doi:10.1002/14356007.a19_421

Langeveld, C. P., & Ten Wolde, K. W. (2013). Phosphate recycling in mineral fertiliser production. In International Fertiliser Society Proceedings 727 Leek, ISBN 978-0-85310-364-6.

Lide, D. R. (2008). CRC Handbook of Chemistry and Physics (89th ed.). CRC Press.

Martí, N., Pastor, L., Bouzas, a, Ferrer, J., & Seco, a. (2010). Phosphorus recovery by struvite crystallization in WWTPs: influence of the sludge treatment line operation. Water research, 44(7), 2371–9. doi:10.1016/j.watres.2009.12.043

Ronteltap, M., Maurer, M., & Gujer, W. (2007). The behaviour of pharmaceuticals and heavy metals during struvite precipitation in urine. Water research, 41(9), 1859–68. doi:10.1016/j.watres.2007.01.026

Schaum, C., Cornel, P., & Jardin, N. (n.d.). Phosphorus Recovery from Sewage Sludge Ash – A Wet Chemical Approach, 583–590.

Schick, J., Kratz, S., Adam, C., & Schnug, E. (2009). Techniques for P-recovery from waste water and sewage sludge and fertilizer quality of P-recycling products. In Phosphorus Recycling and good Agricultural management Practice.

Schipper, W. J., Klapwijk, a, Potjer, B., Rulkens, W. H., Temmink, B. G., Kiestra, F. D., & Lijmbach, a C. (2001). Phosphate recycling in the phosphorus industry. Environmental technology, 22(11), 1337–45. doi:10.1080/09593330.2001.9619173

Schultz, H., Bauer, G., Schachl, E., Hagedorn, F., & Schmittinger, P. (2000). Potassium Compounds. In Ullmann’s Encyclopedia of Industrial Chemistry. doi:10.1002/14356007.a22_039

STOWA. (2012). Struviet productie door middel van het airprex proces (2012th–27th ed.). Amersfoort: Stichting Toegepast Onderzoek Waterbeheer.

Ten Wolde, K. W. (2012). Phosphate fertilizer from Sewage Sludge Ash. University of Twente.

Van Vuuren, D. P., Bouwman, a. F., & Beusen, a. H. W. (2010). Phosphorus demand for the 1970–2100 period: A scenario analysis of resource depletion. Global Environmental Change, 20(3), 428–439. doi:10.1016/j.gloenvcha.2010.04.004

Yamamoto, T., Tsutsui, T., Nonaka, T., Kobayashi, S., Nishiguchi, A., & Yamane, I. (2006). A quantitative assessment of the risk of exposure to bovine spongiform encephalopathy via meat-and-bone meal in Japan. Preventive veterinary medicine, 75(3-4), 221–38. doi:10.1016/j.prevetmed.2006.03.003

Authors

C.P. Langeveld; K.W. ten Wolde

ICL Fertilizers FE

Fosfaatweg 48

1013 BM Amsterdam

The Netherlands

The Budenheim Carbonic Acid Process

An environment friendly process for recovering phosphates from sewage sludge

Rainer Schnee, Rüdiger Wissemborski, Eva Stössel

Budenheim

1. Introduction

Phosphorus is an essential component of every living being and cannot be substituted by other substances. In fertilizers, phosphate is one of the limitative elements for growth of a plant. Estimates about the depletion of phosphate rock reserves extend between 40 to 400 years.

The demand for phosphorus as fertilizer will grow in the next years, especially in the developing countries. Phosphorus reserves are highly polluted with uranium and cadmium accumulated in soils. Also, the mining of the phosphate rock causes a lot of environment pollution and requires high energy input.

Germany has no phosphate reserves of its own and it depends completely on phosphate-imports, from countries like Morocco. This causes increased interest into the research and development of alternative sources of phosphates, with Sewage sludge being one possible source for phosphorus. Each person loses approximately 1.8 g per day of phosphate from which the major part is removed from the waste water in waste water treatment plants and accumulated in sewage sludge. The use of sewage sludge as fertilizer is discussed because of the pollutants it contains, like residues of drugs or heavy metals.

Thus, decrease of the dependency on import and increase of phosphorus availability calls for invention of an environment friendly process for recovering phosphates from sewage sludge.

2. The Budenheim process

The described process for recovering phosphate was invented by the Chemische Fabrik Budenheim KG (named “Budenheim”). The Carbonic Acid Process at

Budenheim focuses mainly on the environment-friendly and sustainable procedures with no addition of heat or chemicals. To run the Budenheim process is possible even on waste water treatment plant with phosphate removal by iron-compounds.

This process uses only carbon dioxide to extract the phosphates which is recycled and reused and hence, it is an environment friendly process with no harmful exhausts.

3. Technical function of the Budenheim process

During the process the phosphates are extracted from the sewage sludge in a carbon dioxide-reaction. The used carbon dioxide can be recycled during the process, so there are no carbon dioxide emissions. The use of other chemicals for the extraction-step is not necessary.

Carbon dioxide is brought into the system of sewage sludge and water under pressure. The carbon dioxide dissolves in the water and reacts to carbonic acid. The pH value in the reaction vessel depreciates and the phosphates in the sewage sludge are resolved. The sewage sludge is then separated in a filtration unit where the carbon dioxide and thereby the phosphates remain dissolved in the solution.

Later, the dissolved phosphates are precipitated by outgassing the carbon dioxide. After drying the phosphates a phosphate-rich fertilizer can be produced.

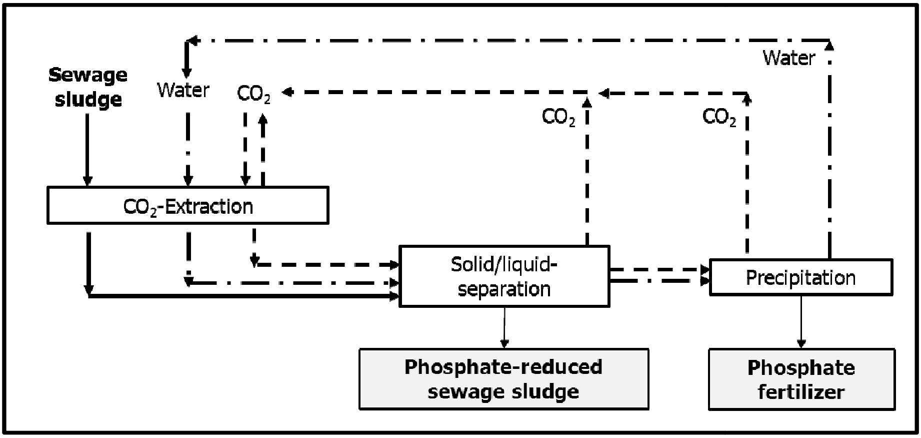


Figure 1: Flow Chart of the Budenheim Carbonic Acid Process

The carbon dioxide is captured, compressed and reused for the reaction in the pressure vessel. The process water used for conditioning the sewage sludge and

Carbon dioxide are recycled and reused. So there are no environment-critic emissions of exhaust-air or waste-water.

Because of the Phosphate-recovery, energy can be saved in the next processing steps like drying and combustion of the sewage sludge. Currently about 50% of the phosphates contained in the sewage sludge can be recycled in the Budenheim Process.

The sewage sludge which is resting after the Budenheim Process has low phosphate content and can be used in the building-material-industry. Very high phosphate-content prevent the usage of sewage sludge. In the cement industry, there is instability of the produced materials due to high phosphate content. In the first step of the process, the nutrients are separated and later the sludge can be used in the cement-industry. Another positive aspect is the increase in the calorific value due to the presence of the non-combustibles in the sewage sludge which are separated before combustion.

4. Innovative aspects of the Budenheim process

The Budenheim process is the first process for the recovery of phosphates from sewage sludge which uses environment friendly carbonic acid for the extraction. The process was patented by Budenheim.

The major aspect is the recycling of the carbon dioxide during the process. The carbon dioxide is captured, compressed and used again for the extraction process. So there are no climate-relevant emissions in the Budenheim-process.

In the Budenheim Process all kind of sewage sludge can be used, even from waste water treatment plants with phosphate removal by iron compounds. So there is no need to switch the P-elimination to biological Phosphate-elimination.

The Budenheim Process uses only carbon dioxide to resolve the phosphates. It is much more environment friendly than using chemicals like sulphuric acid and is more cost effective at the present scenario. The Budenheim Process does not require thermal- or chemical addition for the extraction of phosphates.

5. Preliminary studies

At the beginning of the project experiments were conducted in the laboratory of Budenheim. The Budenheim-invention-announcement “Phosphate-recovery from sewage sludge” was received by the German patent agency on august, 11th in 2009 (DE102009020745A1). The research-statement was sent by the German patent agency on February, 10 in 2010. This statement and the following correspondence prove that no foreign property rights were hurt and that the process is new and inventive.

Professor Dr. Glinka wrote an expertise about the “Development of a totally new process for sustainable recovery of phosphates through environment-friendly carbon dioxide extraction”. It questions different aspects of the process and as conclusion the Budenheimer process is a qualified possibility for our supply with phosphates.

The process was tested in the Budenheim laboratories considerably. After this, it could be shown that the process can even work in a larger scale. In co-work with the Fraunhofer association (Fraunhofer Institut für Chemische Technologie (Fh ICT)) an experimental plant was installed in Pfinztal, Germany. This was the first scale up. The extraction reactor has a volume of 20 litres.

Based on the experiences in Pfinztal a second plant was built in Budenheim with a bigger reaction volume of 50 litres. Both experimental plants were aided by the Investitions- und Strukturbank in Rhineland-Palatinate.

6. Current running experimental plant in Budenheim

The following picture shows the current running experimental plant in Budenheim.

The sewage sludge/water-suspension is carried in the extraction vessel using the dosing pump.

At the bottom of the extraction vessel, carbon dioxide is leaded. Extraction and separation vessel have a volume of 50 litres. In the extraction vessel pressure, temperature, pH value and fluid level are measured. An agitator can be used if needed.

After the reaction time, the sewage sludge/water-suspension is separated by filter elements and the filtrate is lead into the separation vessel, which has a pressure measurement unit.

Extraction vessel and separation vessel have a pressure relief valve, to avoid the excess of the allowed total pressure. The pressure can be controlled at the vessel using the valves. Valves are also present at the bottom of the vessel for total depletion. Few months ago, a third vessel was installed with a volume of 200 litres.

Figure 2: Experimental Plant in Budenheim

7. Pilot plant

The planned pilot plant at the waste water treatment plant is the continuance of the research project where the conclusions from the two experimental plants is realised and the process is optimised. In the new project, the technical expertise should be converted in a lager plant in a Scale-Up-process. At the pilot plant the technical expertise can be verified and the condition for a full production unit can be collected.

Beneath the phosphate recovery from sewage sludge, the possibility of recovering other substances from the sludge attracts more attention. From the expertise knowledge in the operation of the pilot plant, a full-scale industrial plant can be planned with detailed information about financial structure and cost-effectiveness.

It could be shown that the use of sewage sludge leads to significant higher phosphorus profits compared to the use of sewage sludge ashes. For this reason, it is reasonable to build the plant near the waste water treatment plant to avoid unnecessary transportations and thereby reduced emissions and costs.

Different reasons argue for the construction of the pilot plant for phosphate recycling at the waste water treatment plant in Mainz-Mombach in Rhineland-Palatinate in Germany. First, all laboratory experiments were performed with sludge from the waste water treatment plant in Mainz-Mombach, which were provided kindly from the waste water treatment plant to Budenheim.

The geological nearness to Budenheim is another interesting reason for the construction of the pilot plant in Mainz-Mombach. The people in power at the waste water treatment plant seem to show interest in the project.

The pilot plant will have a reaction volume of round about 1000 litres. The normal business of the waste water treatment plant will not be affected by the pilot plant. A change in treating the waste water is not necessary for the Budenheim Carbonic Acid Process.

8. Environmental relief

In the following sectors environmental reliefs will probably be reached by realising the Budenheim process.

Reduction of transport routes

The fertilizer out of sewage sludge substitutes fertilizer from conventional phosphate mines. The greatest phosphates mines are currently in Morocco in Northern Africa. By saving the mineral fertilizers, the necessary transport routes are considerably decreased. Otherwise the transport routes for a part of the sewage sludge fell away, which is necessary to transport the sewage sludge to the treatment plants.

Substitution in the cement industry

The phosphate-extracted sewage sludge-residue is a CO_2-neutral combustion residue with characteristics similar to cement. This allows a partly substitution of the aggregates in the cement industry. By using the CO_2-neutral sewage sludge residue, considerable amounts of carbon dioxide can be saved. Before using the sewage sludge residue extensive analyses concerning the adequacy have to be done. The Budenheim Process delivers also an input for climate-protection.

Soil protection

Beneath these quantifiable environmental aspects, there are other environmental aspects of the Budenheim Carbonic Acid Process. The direct sewage sludge application on agricultural used areas can cause soil pollution because of the harmful substances contained in the sewage sludge. By extracting the phosphate compounds out of the sewage sludge which can be used as fertilizer, the harmful substances can be disposed.

Furthermore the conventional phosphate rock mining causes damages on the natural ecosystem, which could be reduced by using the phosphate potential of the sludge. Another aspect is the reduced input of uranium and cadmium which is contained in the conventional phosphate raw material.

Reduction in sewage sludge-transport

Because of the application of the sewage sludge directly at the waste water treatment plant, the climate- and environmental pollution caused by sewage-sludge transports are reduced.

Reduction in the amount of sewage sludge that goes into incineration

By extracting the phosphates of the sewage sludge, the amount of non-combustible sludge decreases. The amount of sewage sludge that has to go into a further treatment, like drying or incineration, decreases which saves costs and energy for combustion.

9. Characteristics of the product

The Budenheim Carbonic Acid Process produces a phosphate-rich fertilizer. Detailed investigation about the plant availability will started in April 2013. Furthermore the possibilities of blend the product in fertilizer specialities are investigated in cooperation with the fertilizer specialist Klose.

In cooperation with Klose the end-product should be included in special fertilizers, which conform to the particular requirements of the customers. In the Budenheim Carbonic Acid Process a fraction wise precipitation is possible. This leads to the possibility to fit the fertilizer to the customers' requirements.

10. Technical and economic risks

One aim of the project is keeping the environmental impact of the process as low as possible. This concludes a reducing of environment-relevant waste waters and emissions. A part of the concept is that the used water and the carbon dioxide are recycled. The carbon dioxide can be compressed and reused for the following extractions. In this way, climate change-relevant emissions can be reduced or avoided completely.

Problems in the daily system operation may occur because of the idea of cycle all water and carbon dioxide flows. At the current point of development no negative effects could be seen, but the size of the reaction vessel is maybe too small to see the caused effects. Probably the cycle-wise process flow leads to accumulation of problematic substances in the plant.

This effect couldn't be seen at the experimental plant yet, but it may occur when greater amounts of sewage sludge are treated in the pilot plant. Because of this, there have to be analysis of all relevant parameters to recognise precipitation, for example of heavy metals in time.

The cycle-wise process flow of the used carbon dioxide can also cause problems, when contamination of the gas occurs after some extraction steps. The influence of this factor can be relevant for the operation unit and have to be controlled in analyses of water and gas flows.

11. Assignability of the technology

We expect that the technology can be applied on many waste water treatment plants in Germany but also worldwide. In the current state of knowledge, the implementation of the Budenheim Carbonic Acid Process is possible even on waste water treatment plants with Phosphorus-removal by iron compounds.

It is possible to conform the process to different sizes of waste water treatment plants.

12. Conclusion

By extracting the phosphorus out of the sewage sludge before incineration, the co-incineration for example in cement plants is still possible. The necessary capacities for pure mono-incineration are in Germany not available. Therefore the co-incineration makes sense when the phosphorus is taken out of the sludge before incineration.

The Budenheim Carbonic Acid Process is one of the recycling processes which are part of the P-REX-study. In this programme Life Cycle Assessments are conducted.

A phosphate reduction in the sewage sludge of 50% is already realised. A phosphate recovery rate of 60 to 70% is one of the long-term objectives.

In tests the plant availability of the Budenheim recycling-phosphate is tested. The tests are currently running at the University of Bonn.

The aim of the research of Budenheim is a low-polluted, plant available fertilizer and a marketable price.

References

[1] Umweltbundesamt, Klärschlammentsorgung in der Bundesrepublik Deutschland, 2012

[2] LAGA, Bund/Länder-Arbeitsgemeinschaft Abfall, „Bewertung von Handlungsoptionen zur nachhaltigen Nutzung sekundärer Phosphorreserven“, 2012

[3] Homepage of P-REX: http://www.p-rex.eu/

[4] Scholz, R.W. Wellmer, F.-W. (2013), Approaching a dynamic view on the availability of mineral resources: what we may learn from the case of phosphorus? Global Environmental Change, 23, 11 – 27

Authors

Dr. Rainer Schnee

E-Mail: rainer.schnee@budenheim.com

Tel.: 06139 – 89 206

Rüdiger Wissemborski

E-Mail: ruediger.wissemborski@budenheim.com

Tel.: 06139 – 89 368

Eva Stössel

E-Mail: eva.stoessel@budenheim.com

Tel.: 06139 – 89 543

Chemische Fabrik Budenheim KG

Rheinstraße 27

55257 Budenheim

Phosphate Recovery from Wastewater with Engineered Superparamagnetic Composite Particles using Magnetic Separation

Carsten Meyer a), Asya Drenkova-Tuhtan a), Heidrun Steinmetz a), Karl Mandel b),c), Gerhard Sextl b),c), Frank Hutter b), Carsten Gellermann b), Anja Paulus d), Matthias Franzreb d)

a) University of Stuttgart

b) Fraunhofer Institute for Silicate Research, Würzburg

c) University of Würzburg

d) Institute of Functional Interfaces, Karlsruhe Institute of Technology (KIT)

1. Introduction

Phosphorus (P), needed by every living organism, is a non-substitutable element. There are also no substitutes for phosphate in agriculture. However, the reserves of easily mineable and low-polluted phosphate minerals are projected to last for only about 90 years. Therefore, methods to recover phosphate from secondary sources have to be developed. With about 60,000 t P/a (Germany) the highest potential for recovery can be found within the municipal wastewater. Between 20% and 40% of the „primary phosphorus“ used in fertilizers could be substituted by “secondary phosphorus” recovered from wastewater.

As a contribution to the existing technologies, this study proposes a novel idea to use magnetic ion exchange particles for the recovery of phosphate directly from wastewater streams. The designed ion exchanger particles, homogeneously dispersed in water, adsorb phosphate selectively, and can be easily separated from the water phase in the gradient of a magnetic field. Subsequently, the ion exchanger particles can be regenerated in an aqueous solution, wherein phosphate is recovered. The regenerated magnetic particles can be reused. This method offers several advantages compared to conventional ion exchange column techniques. The most important advantage is the avoidance of clogging and fouling. Furthermore, due to the small size of the particles, myriads of adsorption spots and shorter diffusion pathways are provided for the uptake of the target substance. An additional benefit is the magnetic solid-liquid separation which is faster than sedimentation or filtration and in any case more selective since only the magnetic fraction is extracted.

2. The Idea - Phosphate Recovery from Wastewater with Superparamagnetic Composite Particles

The synthesis of superparamagnetic microparticles (Mandel et al., 2012) and their modification with layered double hydroxide ion exchangers (Mandel et al., 2013) were reported recently. Superparamagnetism is a nano-effect of magnetism that can be used to switch the magnetization of a material "on" or "off" by applying or removing an external magnetic field.

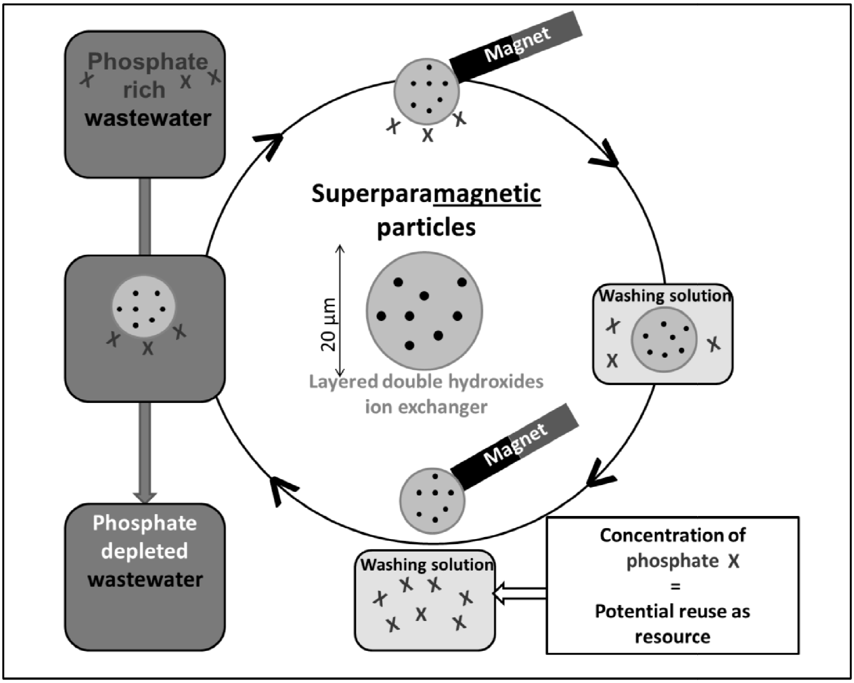


Figure 1: Principle of the phosphate recovery from wastewater by superparamagnetic composite particles

This ensures that the particles can be easily separated when magnetically "switched on", but they can also be homogeneously dispersed in an aqueous medium, without facing the problem of magnetic agglomeration, when the external magnetic field is removed. The principle of the phosphate recovery from wastewater by superparamagnetic composite particles, their recovery both from the wastewater and the washing solution is shown in Figure 1. Figure 2 illustrates the magnetic separability of the particles from the aqueous phase, here with the help of a handheld magnet.

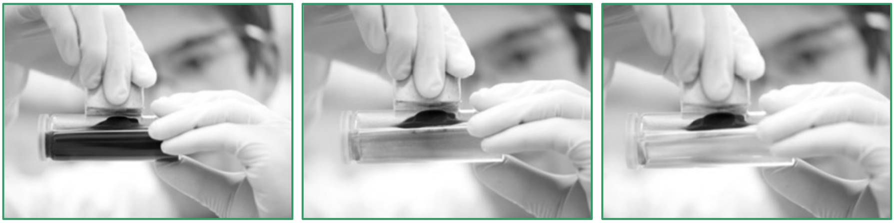


Figure 2: Separability of the particles from the aqueous phase

The ion exchanger on the particle’s surface (layered double hydroxides (LDH)), is a mixture of 2-, 3- and 4-valent metal ions as metal hydroxides, which form layered structures similar to the natural mineral brucite (Rives and Ulibarri, 1999).

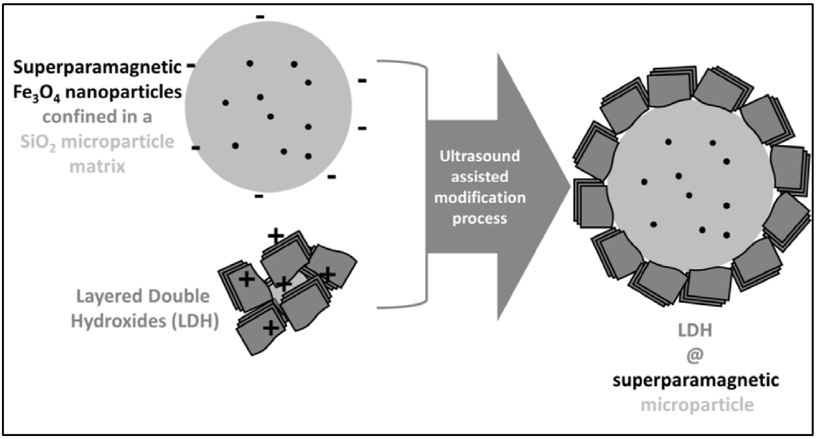


Figure 3: Superparamagnetic nanocomposite microparticles

Figure 3 shows the superparamagnetic nanocomposite microparticles, consisting of magnetite nanoparticles in a silica matrix. As a phosphate selective ion exchanger the layered double hydroxides (anionic clays with brucite-like structure) are deposited on the surface of these particles by an ultrasound-assisted technique.

LDHs were reported to be promising selective ion exchangers for phosphate (Seida and Nakano, 2002; Chitrakar et al., 2005; Kuzawa et al., 2006; Chitrakar et al., 2007;

Goh et al., 2008; Cheng et al., 2009; Xu et al., 2010; Chitrakar et al., 2010) but, according to our knowledge, a practical way of recovering the material for further reuse has not been suggested yet. The design of a fixed bed column seems to be difficult as LDHs are typically in the form of loose, micron sized flakes, therefore, the idea of using magnetic carriers on which the ion exchange material can be attached and suspended in wastewater is considered as a smart and attractive solution. In this work various layered double hydroxide modifications were screened to determine the most effective system for selective phosphate uptake from municipal wastewater. For this system the influence of different reaction parameters was studied in detail. Various desorption solutions were tested to enhance the recovery of phosphate and the regeneration of the particles. The possibility to reuse the particles in 15 cycles and to enrich the recovery solution with phosphate was demonstrated on a lab-scale.

Furthermore, a larger scale test with 125 L wastewater in 5 cycles was also performed using high-gradient magnetic filtration (HGMF). Results from this test are not being represented here.

3. Results and Discussion

3.1 Magnetic Separability

The magnetic separability of particles with and without LDH modification was tested in a lab-scale magnetic separator column (Figure 4). Even particles modified with 40 wt% LDH dispersed in wastewater, despite the increased load of non-magnetic material, were well separable (> 80-95%), even at a flow velocity of 15 m/h. Generally, it was observed that the separability improved with increasing concentration of the magnetic particles in water (up to > 95% at 100 mg/L Fe_{tot}), probably due to mutual magnetic agglomeration effects. With respect to real applications, such higher Fe concentrations are more relevant, and therefore good separation efficiencies can be expected.

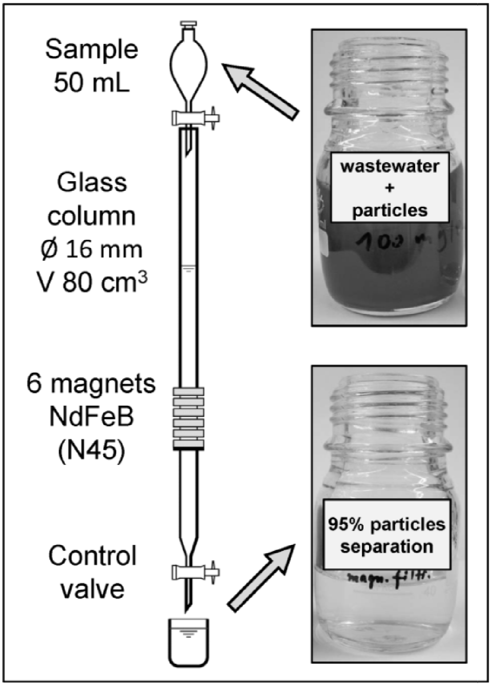


Figure 4: Schematic of the laboratory test system

3.2 Phosphate Adsorption

Figure 5a summarizes the comparison of the performance of the different LDH-magnetic particle-modifications achieved with 200 mg/L LDH at pH 7-8 after 24 h reaction time with municipal wastewater (lab-scale, 100 mL). Besides the LDHs, a zirconia precipitate was also deposited onto magnetic particles as this material is supposed to have a good phosphate affinity (Sarkar et al., 2010). However, this was not observed in our work and due to its low selectivity, the Zr-based precipitate on magnetic particles was not investigated further. On the other hand, Zr-doped LDHs showed improved phosphate adsorption compared to their undoped equivalents, reaching a maximum of the specific phosphate uptake at 29.5 mgP/gLDH for the MgFe-Zr LDH system. This result is comparable with literature values for pure MgFe-Zr LDH (Chitrakar et al., 2010). However, good phosphate adsorption does not necessarily imply good selectivity. Therefore, the effect of other potentially competing anions in wastewater was studied as a further criterion for selection of the most efficient particle system.

The results presented in Figure 5b show a significant simultaneous total carbon uptake, predominantly total inorganic carbon (TIC), followed by phosphate and some adsorption of sulfate and nitrate in all systems. In general, dissolved carbon, usually in the form of HCO_3^-, may come from CO_2 which is dissolved in the solution and can be easily intercalated into the LDH structure and compete with phosphate for the adsorption sites (Chitrakar et al., 2010; Park et al., 2010). In addition to anions, total organic carbon (TOC) was also measured to analyze the competing effect of residual organic substances in the wastewater and it was found out that the adsorbed TOC on the particles surface was insignificant (4%). In general, the proposed phosphate recovery method is recommended for application in pre-treated wastewater, i.e., at the effluent which is almost free of organics but rich in dissolved phosphate (assuming no phosphorus precipitation or biological elimination has taken place in any of the earlier treatment steps). MgFe LDH seems to have the best phosphate affinity (45% of the total adsorbed species) but its specific uptake was approximately 30% lower (20 mgP/gLDH) than the Zr-doped version of the same material. At the same time, MgFe-Zr LDH had a similar selectivity performance (41%) but much better adsorption capacity (29.5 mgP/gLDH). The anions affinity for this system was found to decrease in the following order: TIC (HCO_3^-) > HPO_4^{2-} > SO_4^{2-} > NO_3^- > F^- and Br^-.

MgFe-Zr LDH on magnetic particles seems to be the most promising combination, therefore, this system was chosen for further in-depth investigation and optimization of the phosphate recovery process.

Figure 6 illustrates the specific phosphate adsorption (mgP/gLDH) from the liquid phase on the LDH surface at various contact times and three different pH ranges (4.5-5; 5.5-6 and 7-8). In order to enhance the reaction kinetics and the adsorption efficiency, LDH concentration was increased up to 400 mg/L, corresponding to 1 g/L particles (40 wt% LDH@magnetic particles). There is a rapid phosphate adsorption in the first hour and equilibrium is reached after approximately 2 hours contact time for pH 4.5-5 and pH 5.5-6. Adsorption at pH 7-8 is much slower and the system is getting close to equilibrium after more than 6 hours of reaction. The fastest kinetics was observed at pH 4.5-5 where more than 90% of the total phosphate was already adsorbed within the first 45 minutes and at equilibrium a capacity of 23 mgP/gLDH was achieved. It was possible to fit the kinetics data with a pseudo-second-order model, developed by Ho and McKay for describing the sorption of divalent metals (Ho and McKay, 2000).

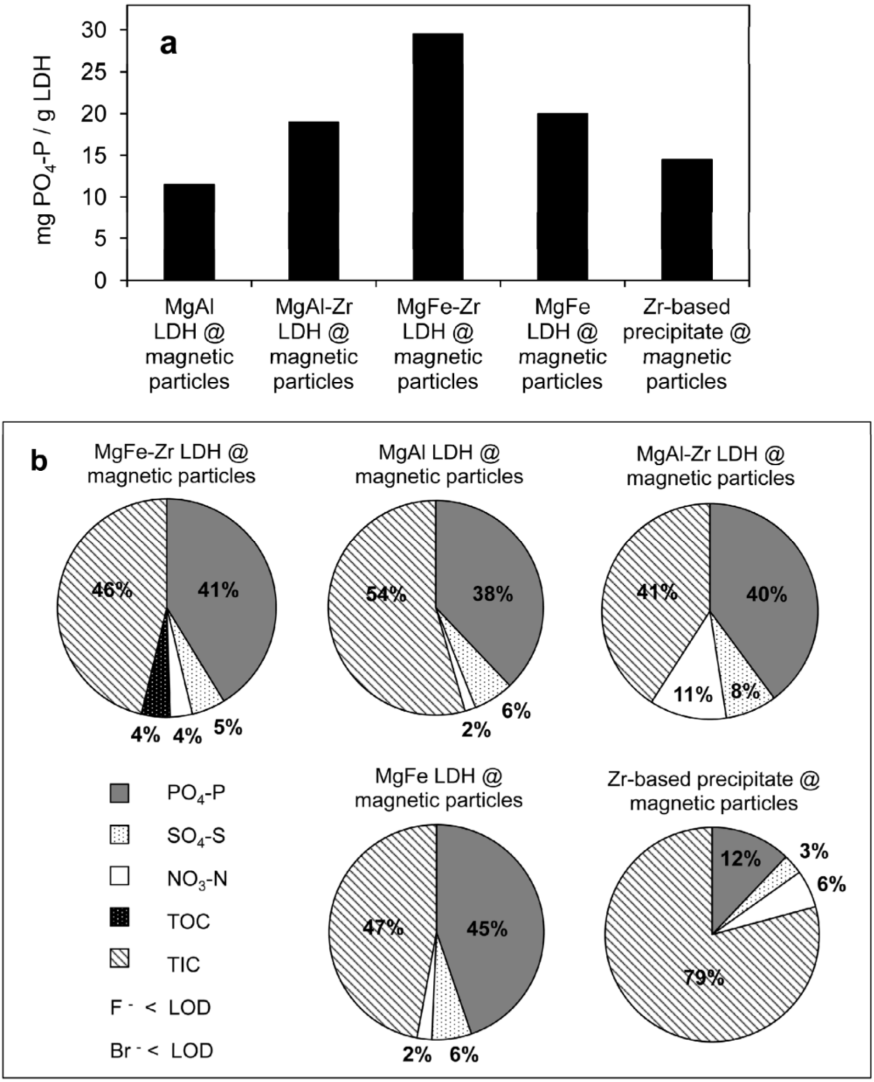


Figure 5: Test results of various LDH-magnetic particle-modifications, a) Phosphate affinity b) Selectivity of anions and uptake of carbon (TOC, TIC)

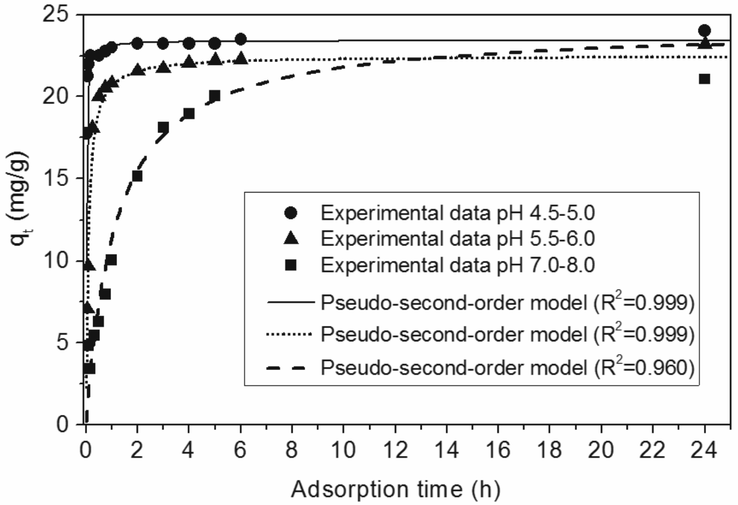


Figure 6: Specific phosphate adsorption on the LDH surface at various contact times and pH ranges

3.3 Phosphate Desorption

In literature various types of solutions are suggested for phosphate desorption and regeneration of LDH systems (Park et al., 2010; Cheng et al., 2009; Kuzawa et al., 2006; Chitrakar et al., 2005). Most studies implied the use of an alkaline medium, such as NaOH, as the most important precondition for phosphate recovery due to the high concentration of OH^- ions, leading to reverse ion exchange and regeneration of the LDH. In this study several combinations of solutions (NaCl, NaOH, $NaHSO_4$, $NaHCO_3$ and NaOH + NaCl) with different molarities have been tested. The phosphate loaded particles were exposed to each solution at different pH values for 1 hour. In conformity with the theory, the recovery of the phosphate was found to improve with higher pH.

Furthermore, the addition of NaCl increased the ionic strength and enhanced desorption. The highest desorption rate (98.2%) was achieved with the combination 1M NaOH + 4M NaCl at pH 12.8. Comparably good (95.6%) was the performance of 1M NaOH + 1M NaCl at pH 12.9, which was selected as the standard solution for the following experiments.

3.4 Reusability of Particles

One of the main goals regarding the design of the composite particles was their potential reusability, tested within 15 adsorption/desorption cycles in two 1 L reactors with two different desorption modes (without or with phosphate enrichment in the desorption solution). The reaction conditions were adjusted according to the best results from the preliminary experiments, i.e. particle concentration in each reactor was 1 g/L (400 mg/L LDH), pH 4.5 and adsorption contact time 1 hour. Desorption time was 30 min in 1M NaOH + 1M NaCl in a separate 1 L reactor.

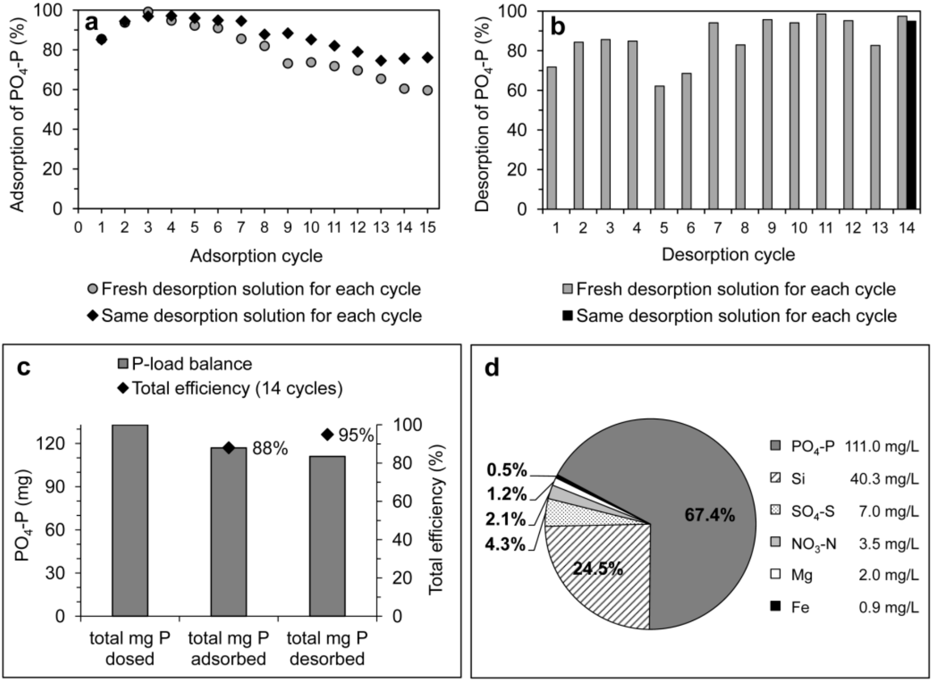


Figure 7: a) Phosphate adsorption efficiency as a function of treatment cycles; b) Phosphate desorption efficiency as a function of treatment cycles; c) P-load balance and total performance of the system; d) Purity of the enriched phosphate solution, leaching of the particles' composite materials and desorption of other anions

Figure 7a shows the influence of the desorption conditions on the phosphate adsorption efficiency in both reactors and Figure 7b summarizes the desorption results. Adsorption of 100% corresponds to complete removal of the initial 10 mg/L PO_4-P. Desorption rates were calculated as a ratio of the desorbed to the adsorbed amount of phosphate. In both cases, the maximum adsorption rate of approximately 99% was achieved after 3 cycles. Afterwards a drop in performance was observed, which in the case of the reactor with the same desorption solution was about 20% after 15 cycles, while in the other reactor the loss of adsorption capacity was more distinct. The desorption rates in the reactor with the fresh solution fluctuated between 62% and 98.5%. At the same time, in the other reactor phosphate was cumulatively concentrated by a factor of 11 in the constantly reused desorption solution and measured at the end of the last cycle. Figure 7c summarizes the P-load balance and the total performance of the system with the enriched recovery solution. Considerably high adsorption (88%) and desorption (95% relative to the total amount of P adsorbed) rates were achieved. In fact, 111 mg PO_4-P were recovered, representing 83.5% of the total mass of PO_4-P (133 mg) dosed into the system. The purity of the enriched phosphate solution was also studied to detect any leaching of the particles' composite materials and desorption of other anions. Besides phosphate (111 mg/L PO_4-P), 40.3 mg/L Si and significantly less SO_4-S and NO_3-N were also detected (Figure 7d). The dissolution of other composite elements, such as Mg and Fe, was very low, indicating a relatively good chemical stability of the particles in a highly alkaline medium (pH 12.9).

4. Conclusions

This work presents the application of superparamagnetic microparticles, modified with LDH ion exchangers for magnetic assisted recovery of phosphate from wastewater.

The particles were well magnetically separable on a lab scale. MgFe-Zr LDH showed the highest phosphate adsorption capacity and good selectivity for phosphate ions. Particle concentration of 1 g/L (400 mg/L LDH) and pH 4.5-5 enhanced the phosphate adsorption kinetics, resulting in a maximum capacity of 35 mgP/gLDH at equilibrium conditions.

For phosphate desorption and recovery of the material a solution of 1M NaOH + 1M NaCl and 30 minutes contact time are recommended.

The reusability of the particles in a municipal wastewater matrix was demonstrated for 15 adsorption/desorption cycles on a lab-scale with insignificant drop in performance. 88% of the initial phosphate was adsorbed, and 95% of the adsorbed phosphate was recovered.

An upscaling of the system appears to be very promising and will be subject to further research. E. g. the use of a drum separator with permanent magnets would make the process cheaper compared to the HGMF.

As a further improvement, the LDH system has to be enhanced to allow faster P-adsorption kinetics, even at neutral pH. Thus, the use of chemicals (addition of acid to the wastewater), possibly causing LDH dissolution and subsequent performance drop could be avoided. The suggested improvements would make this method an attractive option for recovery of phosphate directly from wastewater streams.

References

Cheng, X., Huang, X., Wang, X., Zhao, B., Chen, A., Sun, D., 2009. Phosphate adsorption from sewage sludge filtrate using zinc-aluminum layered double hydroxides. Journal of Hazardous Materials 2009 (1-3), 958-964.

Chitrakar, R., Tezuka, S., Sonoda, A., Sakane, K., Ooi, K., Hirotsu, T., 2005. Adsorption of phosphate from seawater on calcinated MgMn-layered double hydroxides. Journal of Colloid and Interface Science 290, 45-51.

Chitrakar, R., Tezuka, S., Sonoda, A., Sakane, K., Ooi, K., Hirotsu, T., 2007. Synthesis and phosphate uptake behavior of Zr^{4+} incorporated MgAl-layered double hydroxides. Journal of Colloid and Interface Science 313, 53-63.

Chitrakar, R., Tezuka, S., Hosokawa, J., Makita, Y., Sonoda, A., Ooi, K., Hirotsu, T., 2010. Uptake properties of phosphate on a novel Zr-modified MgFe-LDH(CO3). Journal of Colloid and Interface Science 349 (1), 314-320.

Goh, K.H., Lim, T.T., Dong, Z., 2008. Application of layered double hydroxides for removal of oxyanions: A review. Water Research 42 (6-7), 1343-1368.

Ho, Y.S., McKay, G., 2000. The kinetics of sorption of divalent metal ions onto sphagnum moss peat. Water Research 34 (3), 735-742.

Kuzawa, K., Jung, Y.J., Kiso, Y., Yamada, T., Nagai, M., Lee, T.G., 2006. Phosphate removal and recovery with a synthetic hydrotalcite as an adsorbent. Chemosphere 62, 45-52.

Mandel, K., Hutter, F., Gellermann, C., Sextl, G., 2012. Modified superparamagnetic nanocomposite microparticles for highly selective HgII or CuII separation and recovery from aqueous solutions. ACS Applied Materials & Interfaces 4 (10), 5633-5642.

Mandel, K., Drenkova-Tuhtan, A., Hutter, F., Gellermann, C., Steinmetz, H., Sextl, G., 2013. Journal of Materials Chemistry A 1, 1840-1848.

Park, K.Y., Song, J.H., Lee, S.H., Kim, H.S., 2010. Utilization of a selective adsorbent for phosphorus removal from wastewaters. Environmental Engineering Science 27 (9), 805-810.

Rives, V., Ulibarri, M.A., 1999. Layered double hydroxides (LDH) intercalated with metal coordination compounds and oxometalates. Coordination Chemistry Reviews 181, 61-120.

Sarkar, A., Biswas, S.K., Pramanik, P., 2010. Design of a new nanostructure comprising mesoporous ZrO_2 shell and magnetite core (Fe_3O_4@mZrO_2) and study of its phosphate ion separation efficiency. Journal of Materials Chemistry 20 (21), 4417-4424.

Seida, Y., Nakano, Y., 2002. Removal of phosphate by layered double hydroxides containing iron. Water Research 36, 1306-1312.

Xu, Y., Dai, Y., Zhou, J., Xu, Z.P., Qian, G., Lu, G.Q.M., 2010. Removal efficiency of arsenate and phosphate from aqueous solution using layered double hydroxide materials: intercalation vs. precipitation. Journal of Materials Chemistry 20 (22), 4684-4691

Acknowledgements

The project was funded by the Baden-Württemberg Stiftung (BioSuPaWert; Umwelttechnologieforschung). Karl Mandel thanks the “Fonds der Chemischen Industrie (FCI)” for financing his work.

Authors

**Carsten Meyer [a)], Asya Drenkova-Tuhtan [a)], Heidrun Steinmetz [a)], Karl Mandel [b),c)], Gerhard Sextl [b),c)], Frank Hutter [b)], Carsten Gellermann [b)], Anja Paulus [d)], Matthias Franzreb [d)]*

[a)] Institute for Sanitary Engineering, Water Quality and Solid Waste Management (ISWA), University of Stuttgart, Bandtäle 2, 70569 Stuttgart, Germany

[b)] Fraunhofer Institute for Silicate Research, ISC, Neunerplatz 2, 97082 Würzburg, Germany

[c)] University of Würzburg, Chair of Chemical Technology of Materials Synthesis, Röntgenring 11, 97070 Würzburg, Germany

[d)] Institute of Functional Interfaces, Karlsruhe Institute of Technology (KIT), Hermann von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

**Corresponding author*

Tel.: 0049.711.685-63754

Fax: 0049.711.685-63729

carsten.meyer@iswa.uni-stuttgart.de

www.iswa.uni-stuttgart.de

The LIGNIMIX technology for stabilization of municipal sewage sludge and liquid manure

János Stadler (Hungary)

1. Concept

The main innovative idea of the process is that adding carbonaceous minerals (lignite or brown coal) to slurries (of biological origin) and subjecting it to radical mechano-chemical impingement, the mixture becomes an evenly peptized suspension. Peptization means that a fully homogeneous colloidal substance is formed which is a stable suspension.

LIGNIMIX technology has in this sense been worked out for stabilizing municipal wastewater sludge or the liquid manure of animal farms.

Both are considered to be environmental pollutants. By applying the wet grinding technology the sludge, unlike with other existing treatments, becomes a stable suspension.

The LIGNIMIX stable suspension can be used as a fuel or applied as a soil conditioner.

2. Realisation of the LIGNIMIX technology

The sludge obtained in the last stage of sewage purification contains 5-6% of dry matter. Before thickening to remove most of the water,

- powdered lignite is added,
- the mixture is continuously subjected to shear stress in a wet grinder (type KAVITRON).

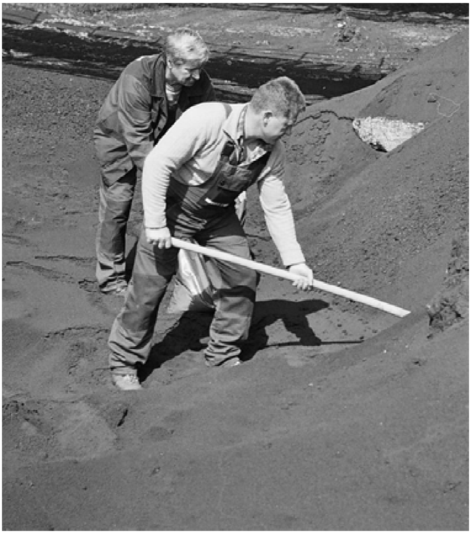


Fig. 1: Collecting lignite powder at the lignite crusher

3. LIGNIMIX wet grinding process

Fig. 2: The experimental wet grinder KAVITRON

Fig. 3: Shear head of the wet grinder set apart

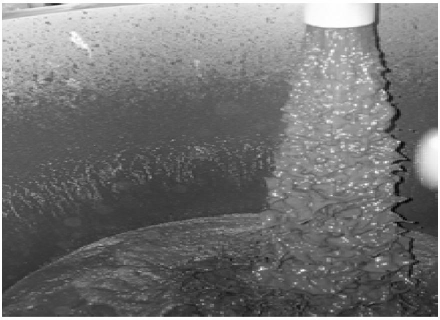


Fig. 4: Suspension is produced

Fig. 5: LIGNIMIX suspension before thickening

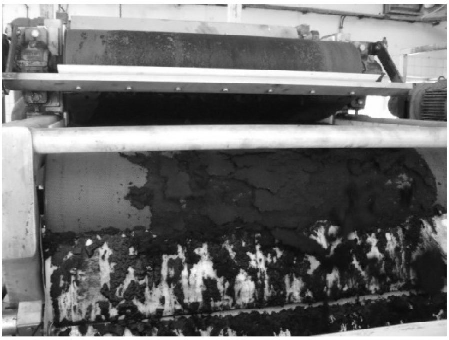


Fig. 6: Partially dewatered suspension after thickening (containing 70-80% water)

4. Positive changes in sludge treatment realised by the LIGNIMIX process

- Lignite disintegrates and gives a homogeneous suspension with the sludge
- The suspension immediately loses most of its bad smell
- When the suspension fully dries, its pathogen count falls by 2 to 5 orders of magnitude

- Desiccation occurs fast and uniformly
- The dry matter obtained (70% or less water) becomes stable (e.g., no rotting, no changes in properties)
- A smell of forest litter will only remain from the odour of the sludge

5. LIGNIMIX products

As the suspension stabilizes, its shelf life becomes unlimited, since the substance obtained can entirely be regarded as carbon (coal)

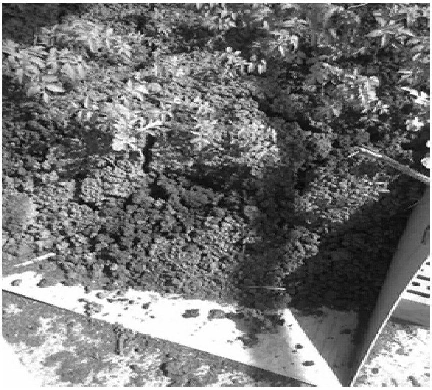


Fig. 7: Desiccated suspension

Fig. 8: Briquetted suspension

6. Utilization of LIGNIMIX suspension

- Fuel: burns exactly as brown coal
- Soil conditioner: a more promising application due to the valuable ingredients worth while recycling into the soil
- Lignite suspensions gradually undergo complete humification
- Compared to sludge treatment by putrefaction, the wet suspension can yield up to 20% more biogas

This was confirmed by tests made in 2005 at the University of Miskolc, Hungary and subsequently by other different research institutes.

7. LIGNIMIX for agricultural use

Expectations:

- increased organic matter
- higher nutrient level
- improved soil structure
- better water retention capability
- humification of the sludge-lignite suspension

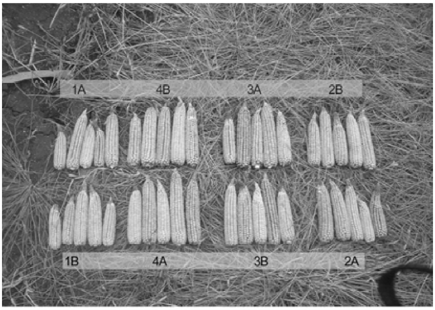
Fig. 9-12: Self-growing of plants in a container (initially foreseen for agricultural tests) full of dried LIGNIMIX suspension after 2 years

8. LIGNIMIX field trials (i)

A parcella területére kijuttatott szennyvíz lignit szuszpenzió Őrbottyán, 2006.06.07.

A kísérlet növényállománya (2B / I parcella) Őrbottyán, 2006.07.09.

A kísérlet növényállománya (kontroll parcella) Őrbottyán, 2006.09.17.



5-5 csőminta a III ismétlés parcelláiról Amót, 2006.10.24.

Fig. 13-16: Maize planted in different soils treated with different doses of LIGNIMIX suspension

It was concluded in the tests that the suspension is well suited to increase the fertility of various soil types and all expectations have been fulfilled.

9. LIGNIMIX field trials (ii)

Fig. 17-20: Saplings of different tree species, grown from the seed and planted in pure sand mixed with increasing amounts of LIGNIMIX suspension

10. LIGNIMIX field trials (iii)

Saplings of different tree species planted in forest soil mixed with different products made from municipal sludge, including LIGNIMIX suspension.

Fig. 21-24: Trial area (above) and field after 4 years (below)

11. Pilot plant experiments to produce LIGNIMIX suspension

- Pig farm in Felsőbabád, Hungary: liquid manure 04.04.2003
- MIVIZ, water purification plant in Miskolc, Hungary municipal sludge 14-15.05.2003
- Pig farm in Felsőbabád, Hungary: liquid manure 04.26-28.2006.
- MIVIZ, water purification plant in Miskolc: municipal sludge 03-05.05.2006

- Water purification plant of the BUDAPEST SEWAGE WORKS Pte Ltd water purification plant in South Pest 2007-2008 (continuously)
- Water purification plant in Gyöngyös, Hungary: municipal sludge June-July 2009 (cont.)
- Biogas production in Dömsöd, Hungary: liquid digestate 18.05.2010
- Water purification plant in Soltvadkert, Hungary: municipal sludge 08 and 09.10. 2010

Large-scale operation has not been implemented to date

LIGNIMIX tests and trials have been carried out to date by:

- UNIVERSITY OF MISKOLC
  date of report : 21.11.2005
- INSTITUE FOR VETERINARY SCIENCES, HUNGARIAN ACADEMY OF SCIENCES
  several reports in 2005 and 2006
- INSTITUTE FOR SOIL SCIENCES AND AGRICULTURAL CHEMISTRY, HUNGARIAN ACADEMY OF SCIENCES
  date of report : 18.01.2007
- HUNGARIAN FOREST RESEARCH INSTITUTE Experimental Branch – Püspökladány, Hungary
  date of report : 17.06.2008
- BUDAPEST SEWAGE WORKS plant in South Pest
  date of report : 11.08.2008
- Dr. ERNŐ FLEIT, expert in ecology
  date of report :06.11.2008
- Water purification plant in Gyöngyös, Hungary
  several reports from 2008 onwards
- BÁLINT ANALITIKA KFT Budapest
  date of report : 09.09.2009
- BAKONY POWER PLANT, Inota Hungary
  date of report : 06.11.2011

LIGNIMIX – Patent and Licence

The LIGNIMIX process is under patent protection.

A Hungarian patent was granted with the priority date of October 10, 2004. (No. 226815)

A European patent is pending.

PCT application No.: 05797337.2

(based on PCT/HU2005/000112)

date of registration: No. 11.10.2005

Based on a licence issued on September 30, 2008 by the Central Statistics Office of Hungary, applications to market the LIGNIMIX suspensions may be submitted under the heading „Production of carbon enriched with sludge of biological origin.

12. Summary

The LIGNIMIX process essentially consists of mixing lignite powder with sewage sludge (or liquid manure) in a powerful wet-grinder unit until the mixture becomes an evenly peptized suspension. Peptization means that a fully homogeneous colloidal substance is formed by powerfully mixing the dry matter of the sludge with the lignite powder. Once dried, this suspension is a fully stabilised carbonaceous substance which practically can be incinerated as a fuel. From a soil property point of view, it qualifies as the source of humus which accommodates itself to the soil to which it has been implemented.

Author

János Stadler

(+36 30) 749-4817

stadler.dr@t-online.hu

Production of bioplastic on a municipal waste water treatment plant

Timo Pittmann, Heidrun Steinmetz

University of Stuttgart

1. Introduction

Common plastic is derived from petrochemicals based on the limited natural resource petroleum. In 2012 the proven crude oil reserves reached 1324 billion barrels, while the daily production was 56.7 million barrels (OPEC 2011). Based on the current reserves to production ratio the proven oil reserves last for about 64 years. Even though this is only a rough estimate, it shows that there will be no more crude oil in foreseeable future.

Plastic derived from crude oil is also responsible for major terrestrial waste problems and most of the oceanic pollution as common plastic is non- or poor biodegradable. The great pacific garbage patch forms the biggest gyre of marine litter and is about as big as France (UNEP 2009). The United Nations Environmental Program (UNEP) estimated that there are 18000 pieces of plastic each km^2, hence the plastic to plankton ratio in this region of the ocean is 6 to 1 (UNEP 2009). Animals mistake the plastic for food and therefore plasticisers and other harmful substances accumulate in the food chain (Wright 2013). Despite these problems the worldwide plastic production reached 280 million tons in 2012 (PEMRG 2012) with only 1.1 million tons of bioplastic (EuropeanBioplastics 2012).

Biopolymers are a possible alternative; they allow the preservation of limited resources and are additionally bio-degradable. Therefore the production of bioplastic includes some advantages and fits to the idea of sustainability.

Polyhydroxyalkanoates (PHA) are among other biopolymers a source for bioplastic production. More than 150 component parts of PHA have been identified so far (Cavalheiro et al., 2009). The possibility for chemical modification of PHA provide a wide range of material properties and an even wider range of use (Zinn and Witholt, 2005; Akaraonye et al., 2010). However, the main raw material for the biopolymer production are starchy plants like maize (Steinbuechel, 2005), constituting the disadvantages of high land consumption, diminishing food resources as well as problems like leaching of nutrients, input of pesticide and soil erosion (Faulstich and

Greif, 2007). Additionally, bioplastic production is rather expensive, with up to 38 % of the costs accounting for the raw material (Lee and Choi, 1997; Choi and Lee, 1999).

So far, municipal waste water treatment plants (WWTP) as alternative raw material and biomass source for the PHA production have not been widely investigated, although they offer the opportunity to compensate the disadvantages of the common PHA production using starchy plants and could turn the WWTP into a bioplastic factory.

Reddy et al. (2008) stated that there is a general possibility to produce PHA from activated sludge. Chua et al. (2003) on the other hand used wastewater as source material and investigated the effect of pH, sludge-retention time (RT) and acetate concentration on the polyhydroxyalkanoates (PHA) production. Hence both showed that the intracellular production of PHA using activated sludge from a municipal WWTP is possible. Chua and Yu (1999) used activated sludge from industrial wastewater treatment to produce biopolymers. Albuquerque et al. (2007, 2010, 2011) provided various results regarding the PHA production from sugar-cane molasses at different operating condition. Nevertheless, none of them performs research on the whole production cycle and all operating conditions for the best PHA yield.

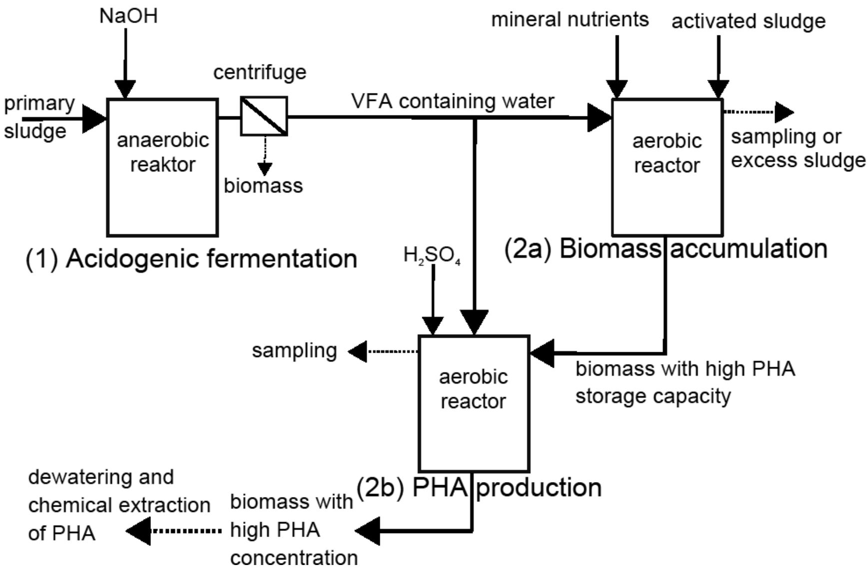


Figure 1: Experimental set-up for the biopolymer production

The aim of this research project is to produce PHA using only material flows of a municipal WWTP. The biological process of PHA production consists of two main steps as displayed in Fig. 1. At first sludge from the municipal WWTP is used to produce volatile fatty acids (VFA) in an anaerobic fermentation process. The following second step converts the VFAs by an aerobic process into biopolymers (PHA) by mixed culture microorganisms based on activated sludge.

In contrast to Bengtsson et al. (2008b) and Morgan-Sagastume et al. (2013) the PHA production process described in this work is designed as a side stream process of a municipal WWTP and does not include the treatment of waste water. Therefore the whole process must consider the polymer production only. Another concern was, how the tested operating conditions or the diversity of the used material flows of a WWTP influence the VFA composition and consequently the kind of PHA produced (Albuquerque et al., 2007). As there is a variation in the composition of the used material flows (sludges) of a WWTP, it is of particular importance to observe their influence on VFA production and composition.

2. Results

2.1 Acidogenic Fermentation

Four different sludges, namely primary sludge, excess sludge, a one to one mixture of primary- and digested sludge and a one to one mixture of excess- and digested sludge from a municipal WWTP were analysed. Primary sludge yielded the highest production of VFAs and the best degree of acidification (DA) (Bengtsson et al., 2008a) with up to 39 % of the raw materials start COD being converted into VFAs. The second best carbon source, a one to one mixture of primary and digested sludge achieved only a DA of 14 %. The composition of the produced VFAs is also of importance as they directly influence the material properties of the PHA produced. The results varied strongly between 24/76/7 (%Ac/%Pro/%Bu) and 100/0/0 depending on the used raw material. Primary sludge produced none butyric acid (Bu) and acetic (Ac) and propionic acid (Pro) in nearly two equal sections (52/48/0). Excess sludge on the other hand produced up to 21 % butyric acid, while the one to one mixture of primary and digested sludge produced the most acetic acid (up to 84 %) of all tested raw materials. As the use of primary sludge resulted in highest DA and showed only small variations in VFA composition under the tested conditions, it was chosen as raw material and used in all further tests.

Afterwards the best operating conditions (temperature, pH, retention time (RT), withdrawal (WD)) to produce VFAs via primary sludge were investigated.

In six out of eight tested combinations a temperature in-crease from 20 °C to 30 °C caused a higher VFA production. The general assumption that the acidification rate is higher at 30 °C than at 20 °C could not be confirmed. Primary sludge under pH-controlled conditions, as the source material with the highest DA, reached its VFA maximum after 7 d at 20 °C and after 9 d at 30 °C. Nevertheless, the fact that the DA of primary sludge under pH controlled conditions at 30 °C was twice as high as the DA at 20 °C should be rated all the more highly as the VFA production at 30 °C lasted only about 30 % longer.

Former studies showed good fermentation results between pH = 5 (Bengtsson et al., 2008b) and 11 (Mengmeng et al., 2009), highly depending on the used substrate. In consequence a range of pH-levels (pH = 6, 6.5, 7, 8, 10) was tested. No big difference in the maximum VFA concentration between pH = 6 and pH = 8 was observed. Although pH = 7 yielded the best result, methane production turned out to be an issue at this pH-value. To prevent methanogenic conditions a pH-level of 6 is to be kept. Consequently further investigations were performed under pH = 6 although it produced about 12 % less VFA.

The VFA composition is highly depending on the pH-level as shown in Table 1. Changing the pH from 6 to 7 caused a constant decrease in the acetic acid ratio. In the same tests, the propionic acid ratio increased, while the butyric acid ratio decreased to zero. At pH = 8 conditions a reverse trend was observed. In comparison to pH = 8, a reduction of acetic acid and propionic acid production was detected at the highest tested pH-level (pH = 10), while the butyric acid ratio increased to the highest level (8 %) observed.

Table 1: VFA composition in dependence of pH (missing to 100% is formic acid)

pH	Ac/Pro/Bu %	DA %
6	45/51/4	29
6.5	37/61/2	29
7	28/72/0	39
8	60/37/3	29
10*	45/31/8	14

Bengtsson et al. (2008b) described the influence of retention time (RT) on the VFA production. To find an approximate RT and to get an idea about how much adapted bacteria are needed in the reactor to produce the most VFAs so called semi-continuous experiments were conducted. Semi-continuous means that the withdrawal was taken out of the reactor at once and the amount of substrate was added to the reactor at once. RT and withdrawal (WD) are related factors, e.g. a RT of 4 d was used when 25 % of the sludge was exchanged every day, 50 % every second day or 75 % every third day. Both, RT and WD influenced the VFA production. With higher WD the VFA concentration was decreasing at all tested RTs. The highest overall VFA concentration was reached at a RT of 6 d with a WD of 25 %. For a later PHA production in a second stage a high VFA mass flow is preferable to a high VFA concentration. A RT = 4 d and WD = 25 % yielded the top mass flow with MF = 1913 $mg_{VFA}/(L\ d)$ at a VFA concentration of 7653 mg_{VFA}/L on average. The variation of RT influenced the VFA composition only marginal. Nevertheless, the variation of WD had an effect. With a WD of 25 % the fraction of propionic acid was about 20 % smaller throughout all tests, while the butyric acid ratio was about twice as much. As a stable VFA composition is necessary for high quality PHA production the possible fluctuation of the VFA composition (due to changing composition of the introduced primary sludge) during the whole test period is of importance. Fig. 2 is exemplary for all semi-continuously operated tests and shows the development of the VFA concentration during the whole test period. After a starting phase of 10 d (not shown in the figure) the semi-continuous operation began. Due to the change in the operation method a transition phase with a decrease in VFA concentration was observed for the first six days of semi-continuous operation. Fluctuations in the VFA concentration between day six and day 44 were due to the changing composition of the introduced primary sludge. Although a fluctuation in VFA concentration was observed, there were only minor changes in the VFA composition. Thus it was possible to show that the variability of the raw material primary sludge did not affect the VFA composition.

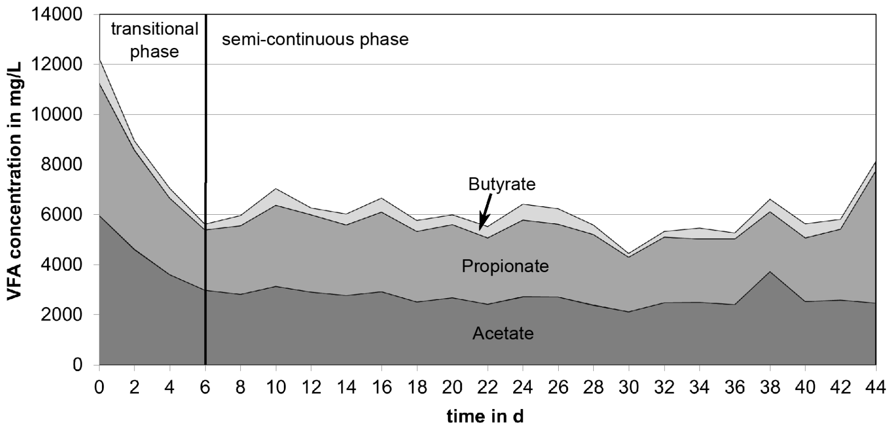


Figure 2: Development of the VFA concentration at RT = 4 d, WD = 50 %

2.2 PHA-Production

The produced VFAs were converted into biopolymers in the second step. As it was a goal of this project to produce PHA by only using material flows of a municipal WWTP a third reactor was necessary (Fig. 1, 2a) to accumulate biomass with a high PHA storage capacity. Therefore a so called "feast and famine" regime was installed. VFAs, nutrients as well as activated sludge were filled in the reactor at the beginning (feast phase). After the VFAs were converted by the bacteria (after about 5 h to 8 h) there was no more substrate in the reactor (famine phase) until next day's substrate feeding. As PHA is a carbon and energy source for the bacteria, the PHA-accumulating bacteria had a selective advantage. Therefore the PHA-accumulating bacteria propagated faster. PHA production tests were conducted after 7 d, 14 d and 21 d of selection to determine the influence of the selection process. The length of the selection process showed no influence to PHA production. The two best results were achieved after 7 d or 21 d of selection.

Various temperatures were tested and 20 °C yielded the highest PHA accumulation. Temperatures of 15 °C and 20 °C were tested, because most of the material flows on a municipal WWTP have temperatures around 15 °C–20 °C all year long. Additionally a temperature of 30 °C was tested, to figure out, if the higher temperature would increase the PHA production. As this was not the case all further tests were performed under 20°C.

It was also tested, if the pH-level has an influence on the PHA production. Therefore tests at pH = 6, 7, 8, 9 and without pH control were conducted. Due to the conversion of VFA into PHA a pH level rise to 9.5 was observed without pH control. The high pH-level decreased the PHA production and only 4.4 % of cell dry weight was achieved. pH = 7 and 8 yielded up to 30 % PHA. Therefore further tests are going to be performed at pH = 7.

Using the received results a mass balance was calculated to estimate the possible amount of biopolymers that can be produced in German WWTPs (Pittmann and Steinmetz, 2013). A WWTP with a daily amount of primary sludge of 1000 m^3 would produce 16.3 t_{VFA}/d. Thus 8.15 t_{VFA}/d would be used for biomass accumulation (Fig 1, 2a) and 8.15 t_{VFA}/d for PHA production (Fig 1, 2b). Reactor 2a would produce 34 t of excess sludge with a high PHA storage capacity every day, which would be used in reactor 2b to produce 10.2 t_{PHA}/d. Consequently an amount of 350,000 t/a – 400,000 t/a of bioplastic could be produced on German WWTPs. This would be about a third of the world wide bioplastic production.

3. Conclusion

From the results, it could be concluded that it is possible to produce high amounts of VFAs with a stable VFA composition on a WWTP. The VFA production and composition is strongly influenced by a pH-level change in the reactor and a short RT and small WD is preferable. The PHA production highly depends on temperature and pH level. About a third of the worldwide bioplastic production could be produced in German waste water treatment plants.

References

Akaraonye, E.; Keshavarz, T. & Roy, I., 2010: Production of polyhydroxyalkanoates: The future green materials of choice Journal of Chemical Technology & Biotechnology, 85, 732-743

Albuquerque, M. G. E.; Concas, S.; Bengtsson, S. & Reis, M. A. M., 2010: Mixed culture polyhydroxyalkanoates production from sugar cane molasses: The use of a 2-stage CSTR system for culture selection. Bioresource Technology, 101, 7112-7122

Albuquerque, M. G. E.; Eiroa, M.; Torres, C.; Nunes, B. R. & Reis, M. A. M., 2007: Strategies for the development of a side stream process for polyhydroxyalkanoate (PHA) production from sugar cane molasses. Journal of Biotechnology, 130, 411-421

Albuquerque, M. G. E.; Martino, V.; Pollet, E.; Avérous, L. & Reis, M. A. M., 2011: Mixed culture polyhydroxyalkanoate (PHA) production from volatile fatty acid (VFA)-rich streams: effect of substrate composition and feeding regime on PHA productivity, composition and properties. Journal of Biotechnology, 151, 66-76

Bengtsson, S.; Hallquist, J.; Werker, A. & Welander, T., 2008a: Acidogenic fermentation of industrial wastewaters: Effects of chemostat retention time and pH on volatile fatty acids production. Biochemical Engineering Journal, 40, 492-499

Bengtsson, S., Werker, A., Christensson, M., Welander, T., 2008b.: Production of polyhydroxyalkanoates by activated sludge treating a paper mill wastewater. Bioresource Technology 99, 509-516.

Cavalheiro, J.M.B.T., de Almeida, M.C.M.,Grandfils, C., da Fonseca, M.M.R., 2009.: Poly(3-hydroxybutyrate) production by cupriavidus necator using waste glycerol. Process Biochemistry 44, 509-515.

Choi, J., Lee, S.Y., 1999.: Factors affecting the economics of polyhydroxyalkanoate production by bacterial fermentation. Applied Microbiology and Biotechnology 51, 13-21.

Chua, H., Yu, P.H.F., 1999.: Production of biodegradable plastics from chemical wastewater - A novel method to reduce excess activated sludge generated from industrial wastewater treatment Water Science and Technology, 1999, 39, 273 - 280

Chua, A. S. M.; Takabatake, H.; Satoh, H. & Mino, T., 2003: Production of polyhydroxyalkanoates (PHA) by activated sludge treating municipal wastewater: effect of pH, sludge retention time (SRT), and acetate concentration in influent. Water research, 37, 3602-11

EuropeanBioplastics, 2012: Bioplastic - facts and figures

Faulstich M., Greiff K. B., 2007: Klimaschutz durch Biomasse (Climate Protection per Biomass), Ergebnisse des SRU Sondergutachtens 2007, Zeitschrift für Umweltschutz und Schadstoff-Forschung 21 UWSF (3)

Lee a.Y., Choi C.Y., 1997: Biosynthesis and Biotechnological Production of Degradable Polyhydroxyalkanoic Acid, Biotechnol. Bioprocess Eng.

Mengmeng, C., Hong, C., Qingliang, Z., Shirley, S.N., Jie, R., 2009: Optimal production of polyhydroxyalkanoates (PHA) in activated sludge fed by volatile fatty acids (VFAs) generated from alkaline excess sludge fermentation. Bioresource Technology 100, 1399-1405.

Morgan-Sagastume, F.; Valentino, F.; Hjort, M.; Cirne, D.; Karabegovic, L.; Geradin, F.; Dupont, O.; Johansson, P.; Karlsson, A.; Magnusson, P.; Alexandersson, T.; Bengtsson, S.; Majone, M. & Werker, A., 2013: Biopolymer production from sludge and municipal wastewater treatment. 1st International IWA Conference on Holistic Sludge Management

OPEC, 2011: Share of World Oil Reserves 2010 OPEC, Vienna, Austria.

Pittmann, T.; Steinmetz, H., 2013: Produktion von Bioplastik auf kommunalen Kläranlagen, Wasser und Abfall 5/2013 37-41

PlasticsEurope Market Research Group (PEMRG), 2012: Plastics – the Facts 2012.

Reddy, S. V.; Thirumala, M.; Reddy, T. V. K. & Mahmood, S. K., 2008: Isolation of bacteria producing polyhydroxyalkanoates (PHA) from municipal sewage sludge. World Journal of Microbiology and Biotechnology, 24, 2949-2955

Steinbuechel A., 2005: Biopolymere und Vorstufen, Kap. 22 des Buches „Angewandte Mikrobiologie“ (Biopolymers and Precursors, Chapter 22 in „Applied Microbiology“), Herausgeber: Garabed Antranikian

United Nations Environment Programme (UNEP), 2009: Marine Litter – A Global Challenge, Nairobi, Kenia.

Wright S. L., Thompson R. C., Galloway T. S., 2013: The physical impacts of microplastics on marine organisms: A review, Environmental Pollution

Zinn, M. & Witholt, B., 2005: Tailored material properties of poly-hydroxyalkanoates through biosynthesis and chemical modification. Adv Eng Mater 7:408-411

Authors

Timo Pittmann, Heidrun Steinmetz

University of Stuttgart

Institute for Sanitary Engineering, Water Quality and Solid Waste Management (ISWA)

Bandtäle 2

D-70569 Stuttgart, Germany

E-Mail: timo.pittmann@iswa.uni-stuttgart.de

EXCEED and EMPOWER Tunisia

Two International Networks for Capacity Building and Research on Water Reuse

Müfit Bahadir

Technische Universität Braunschweig

Extended abstract

Water is one of the 21st century's key development issues. More than one billion people worldwide do not have access to clean drinking water, whilst around half of the mankind do not have suitable sanitary facilities or wastewater treatment. This situation becomes worsen through the consequences of climate change in particular in already drought regions. The ***EXCEED*** and ***EMPOWER Tunisia*** projects at TU Braunschweig address to the MDG 7/C "Ensure Environ-mental Sustainability - Halve by 2015 the proportion of the population without sustainable access to safe drinking water and basic sanitation". These two projects are aiming at to reach this goal through international cooperation on education, capacity building, and joint research.

The Project ***EXCEED – Excellence Centre for Development Cooperation – Sustainable Water Management in Developing Countries*** began 2009 at TU Braunschweig together with 35 partner universities and research centres in developing and emerging countries, and is scheduled for 5 years granted through DAAD. Pioneering research and academic cooperation projects with partners from Latin America, Middle East, Sub-Sahara Africa, and South-East Asia have been developed focusing on sustainable and transferable solutions for each region's predominant water-related issues. The topics cover i.a. water in arid and semiarid regions, use of reclaimed wastewater for irrigation, and water quality and health.

To achieve these goals, the existing study programs at partner universities on sustainable water management at MSc and PhD levels were analyzed and upgraded, new courses initiated for the purpose of further education of scientific and technical staff at universities, enterprises, and public authorities at the respective regions. An International Guest Chair was founded at TU Braunschweig, and guest professors and international scholars were invited as team members for conducting joint research and further education on sustainable water management. Furthermore, an intense exchange of students, post docs, and professors were conducted in all directions

south-north, north-south, and south-south for the purpose of education and research for capacity building. Important measures within EXCEED are summer schools, regional and international workshops, and expert seminars organized for scientific exchange and capacity building; e.g. in 2012 “UNESCO/DAAD/EXCEED Conference on Water in Africa”, “Global Warming and Sustainable Water Management”, “Water, Land, and Food Sovereignty in South-East Asia”, “Water Footprint of Middle East Countries”, “Water Losses Management in Water Supply Systems”, “Water and International Relations”, “Sustainable Flood Risk Analysis and Management”, and several “Training Courses on Water Quality and Testing”.

A spin-off from EXCEED is the Transformation Partnership Project ***EMPOWER Tunisia – Emerging Pollutants in Water and Wastewater*** used for irrigation in Tunisian agriculture that aims at initiating a dialogue at scientific, educational, socio-cultural, and political levels on the most emerging topic in the Middle East “Water and its Scarcity”. Water is essential for the development of the country in terms of food production, health, and prosperity, supporting thereby the transformation processes and political stability through meeting the demands of the population. EMPOWER Tunisia aims at building a network between universities, research centres, stakeholders, and policy makers to monitor the current situation of wastewater reuse in Tunisia and further Arab Countries with an emphasis on emerging pollutants in reclaimed wastewater and irrigated agricultural land, and thereby capacity building for technicians, students, and young researchers.

Almost all Arab Countries belong to the driest regions on earth. Reclaimed wastewater as a non-conventional water resource can partially meet the irrigation water demand in agriculture. However, there is a wide range of wastewater qualities used for irrigation: raw, partially treated, diluted with drainage water, or directly applied in river basins after discharge, secondary, and tertiary treatment. Besides typical wastewater constituents like BOD, COD, TSS, heavy metals, and bacteria, increasing amounts of chemical pollutants are introduced into wastewater resulting in various environmental and health impacts. In particular, “emerging pollutants” like drug residues, musk fragrances, surfactants and their metabolites, and further EDCs and PPCPs are rarely investigated in Arab Countries although being researched in Germany and Europe since 1990s. There is an urgent demand to transfer existing knowledge from developed countries to the developing ones being in a transition state towards democracy like Tunisia.

The objectives and measures of EMPOWER Tunisia are

- (i) improving the state of knowledge on emerging pollutants in water,
- (ii) stock taking of the current situation of emerging pollutants in water resources,

(iii) developing sustainable solutions for the problems of irrigation water pollution,

(iv) identifying the gaps of environmental knowledge and developing adopted solutions,

(v) setting up a database for dealing with emerging pollutants in water for irrigation,

(vi) and dissemination of the results through workshops, stakeholder meetings, and symposia. Since its begin 2012, several workshops under participation of scientists from Germany, France, Greece, Turkey, and all Mediterranean Arab Countries (MENA Region – from Morocco to Jordan) were organized in Tunisia, and several students and researchers trained at TU Braunschweig. They visited also the Braunschweig Wastewater Authority (Stadtentwässerung) and the Sewage Board (Abwasserverband) as reuse of treated wastewater has a long tradition in Braunschweig Region and could serve as a Best Practice Example for the arid and semi-arid countries in MENA. Sampling campaigns in Tunisia for irrigated soils, reclaimed wastewaters, and ground waters are conducted at irrigation sites and analyzed in Tunisia and Braunschweig. These data on emerging pollutants will be introduced along with those from other Arab Countries in an all Mediterranean Basin Database consisting of North Africa, Middle East, and South Europe for taking international environmental measures against emerging pollutants.

In Braunschweig, in Germany, and in Euro-Mediterranean Countries technologies and management structures are established for sustainable use of water and reuse of wastewater that could help Tunisia and other semi-arid countries to develop their own environmentally benign solutions for the valorization of reclaimed wastewater for agriculture and food production.

URLs: http://www.exceed.tu-braunschweig.de/ and
https://empowertunisia.alumniportal.com/

Author

Prof. Dr. Müfit Bahadir

Technische Universität Braunschweig, Institute of Environmental and Sustainable Chemistry

Hagenring 30, D-38106 Braunschweig, Germany, m.bahadir@tu-bs.de

Risk Assessment of the wastewater reuse system of Braunschweig

Wolfgang Seis

Berlin Centre of Competence for Water

Abstract

Risk-based management approaches are more and more used in the water sector and are promoted by the WHO. As a first step towards an overall risk-based management approach of the agricultural wastewater reuse concept of Braunschweig a quantitative microbial risk assessment (QMRA) is conducted. A 1000 trial Monte Carlo Simulation is used for the assessment of microbial risks for fieldworkers and nearby residents. As a tolerable value of risk an additional disease burden of 1 µDALY is set following the current WHO guidelines. Concerning microbial risks risk-based targets are set in terms of additional required pathogen reduction in the STP Steinhof. Based on the model results an additional reduction of 1.5log units is derived for viruses, for which the highest annual risks of infection per person per year (pppy) is calculated in all scenarios.

1. Introduction

In 2006, the WHO published the “Guidelines for the safe use of wastewater, excreta and greywater in agriculture” (WHO 2006). The document emphasizes the potential benefits of agricultural water reuse but also underlines the health risks that might be associated with it, especially concerning microbial infections.

In order to maximize of the benefits water reuse while minimizing adverse effects, the WHO states that “the most effective means of consistently ensuring safety in wastewater use is through the use of a comprehensive risk assessment and risk management approach that encompasses all steps of the process […]” (WHO 2006, p. 16, chap. 2.6, l. 4).

This paper shows how risks related to microbial hazards can be assessed at agricultural water reuse systems using the Braunschweig reuse scheme as a case study.

1.1 The Braunschweig wastewater scheme

In the wastewater treatment scheme of Braunschweig, treated wastewater and stabilized sewage sludge are reused in agriculture. Historically grown, this kind of reuse is practiced for over 50 years (Eggers 2008). The wastewater treatment plant (WWTP) Steinhof treats the wastewater of the city of Braunschweig and surrounding communities and has a total of 350000 population equivalents (PE). The treatment plant includes primary sedimentation as well as activated sludge treatment for the removal of bulk organic carbon. The nutrients nitrogen and phosphorus are partially removed biologically. Two third of the treated wastewater, an average amount of 15,000,000 m³ per year, is used for the irrigation of the 3000 ha of agricultural area of the sewage association Braunschweig (AVBS). The remaining third enters natural infiltration fields as a final treatment step, before it is discharged to surface waters. During summer the digested sludge is mixed with the effluent of STP and is used for the irrigation of agricultural areas, too. About 50-60% of the annually produced sludge is applied to the areas of the AVBS this way (Ripke, personal correspondence). The agricultural area of the AVBS is divided in four districts, in the following referred to as district I-IV.

1.2 Scope and goals

Referring to the WHO publication Water Quality: Guidelines, standards and health - assessment of risk and risk management for water-related infectious disease (Stockholm framework) (Fewtrell and Bartram 2001). Figure 1 illustrates the overall approach on how to develop health-based guidelines and standards for the effective control of microbiological hazards in water and sanitation systems.

At the basis of the Stockholm approach stands the assessment of health risks due to environmental exposure of humans to hazards related to the water system of interest as well as the derivation of tolerable (acceptable) health risks. Subsequently, health-based targets are set taking the current actual health risk as well as the derived tolerable health risk into account. In order to ensure and monitor those targets sound risk management plans have to be developed and, finally, its impacts on the overall public health status to be examined and evaluated.

Systems have to be periodically reassessed as conditions, scientific evidence or the availability of data change. The effectiveness of the implemented risk reduction measures has to be verified and the system might have to be completely reanalyzed if they fail to achieve the set health-based targets. Although the approach focuses on microbial risk for human health it can be readily transferred to environmental impacts and chemical hazards. The present study, conducted within the research project CoDiGreen, aims at supporting the implementation of the described iterative process by demonstrating a methodological approach for the assessment of microbial health risks resulting from agricultural water reuse.

In order to assess the risks resulting from pathogen exposure a quantitative microbial risk assessment for fieldworkers and nearby residents is conducted for selected reference pathogens. Risk is expressed using the DALY indicator (disability adjusted life years). The calculated values are compared to the tolerable level of risk of 10^{-6} additional DALYs per person per year (pppy) following WHO guidelines (WHO 2006). Based on this comparison health based targets are derived as additional necessary log removal of pathogens (performance targets).

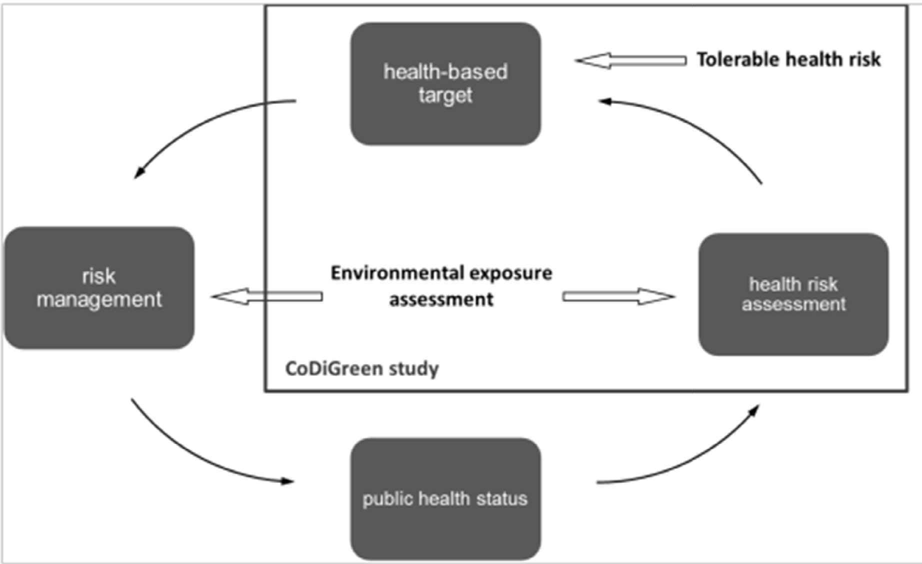


Figure 1: Overall risk management approach outlined in the Stockholm framework (WHO 2006)

2. Methods

In general risk is the product out of the probability of an adverse health effect and the severity of its consequences. Health risk assessment represents a multidisciplinary approach generally consisting of four steps (WHO 2006):

1. ***Hazard identification***: prove of causative relation between a certain chemical or microbial agent and a certain adverse effect for human health and/or the environment.
2. ***Hazard characterization***: After a certain agent is identified as a hazard, the step of hazard characterization collects information on its characteristics, e.g. distribution, physic-chemical properties, main sources of emission (Henning et al. 2010). A crucial point of this step is to determine dose-response relations, or concentration-effect relations.
3. ***Exposure assessment***: The purpose of exposure assessment is to predict the fate of a hazard from its source to the endpoint of interest and the quantity this endpoint is exposed to.
4. ***Risk characterization***: Risk characterization includes all the information of the three previous steps in order to estimate the magnitude of the human health or environmental risk ((Haas et al. 1999), chap. 3). Furthermore, risk characterization evaluates variability and uncertainties within this estimate.

The study focuses on already identified hazards which are typical for the reuse scheme in Braunschweig. Following the general steps of health risk assessment, this paper will be structured in:

- Hazard selection and characterization
- Exposure assessment
- Risk characterization

3. Hazard selection and characterization

At the WWTP Steinhof no microbial parameters are monitored. In order to select suitable reference pathogens for quantitative microbial risk assessment epidemiological data collected by the Robert-Koch-Institute are analysed. The approach follows the logic that the pathogens causing the most cases of illness in a certain area are the ones most frequently found in wastewater. Additionally, enterohemorrhagic E. coli (EHEC) is selected because of an outbreak of EHEC infections in 2011. Based on the data shown in Figure 2 Campylobacter and Salmonella were chosen as reference pathogens for bacteria. Analogously, Norovirus, Rotavirus and Giardia were chosen as representatives for viral and protozoan pathogens.

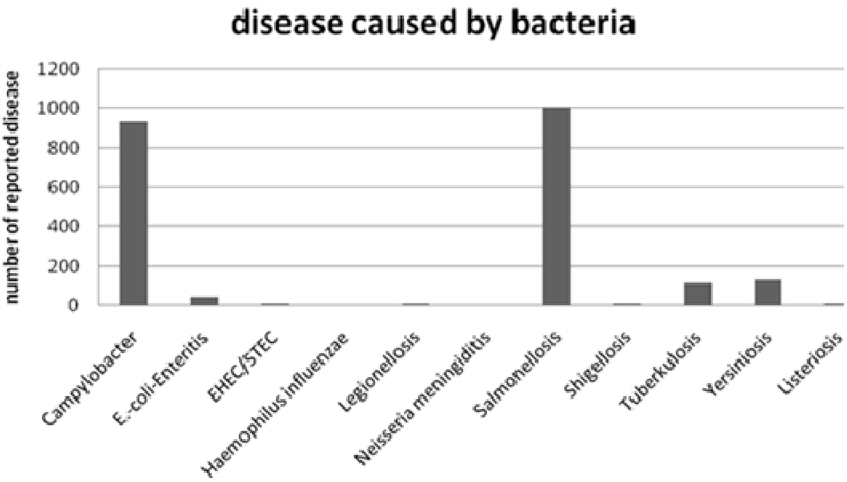


Figure 2: Number of disease incidents caused by bacterial infections. The diagram shows the mean reported number from 2001-2010 in the governmental district of Braunschweig (Robert-Koch-Institut 2011)

3.1 Dose-response relations for pathogens

The dose-response relation concerning pathogens describes a functional relationship between the number of pathogens taken up and the probability of infection. The used functions and parameters for the selected reference pathogens are presented in Table 1.

Depending on the model differences in susceptibility and/or immunity within the exposed population are considered. The exponential model, which is used for Giardia assumes that all pathogens are equally infective and that all exposed people are equally susceptible. Differences in susceptibility are considered using the Beta-Poisson model. For Norovirus a confluent hyper-geometric function is used (Teunis 2008). This function never reaches a value of 1, meaning that it assumes a certain percentage of exposed people to be immune against this kind pathogen.

Table 1: Dose-response modeling parameters used for calculating the probability of infection due to the intake of a specific pathogen dose

Exponential (k), Beta-Poisson parameters (N_{50}, α) , Hypergeometrical $_2F_1$ (a, α, β)					
Pathogen	k	N_{50}	α	a, β	References
Campylobacter		896	0.145		(WHO 2006)
EHEC		1230	0.1778		(Haas et al. 1999)
Giardia	50.23				(Haas et al. 1999), (Rose et al. 1991)
Norovirus			0.04	0.0001, 0.055	(Teunis et al. 2008)
Rotavirus		6.27	0.2531		(Haas et al. 1999), (WHO 2006)
Salmonella		23600	0.21		(Haas et al. 1999)

4. Exposure Assessment

Exposure assessment estimates the dose of pathogens people are exposed to, which is used as an input for the described dose-response models.

Irrigation with treated wastewater can lead to exposure of different population groups via various pathways. In Braunschweig no products are grown which are consumed without further processing. Thus, the exposure route via food intake can be excluded. Furthermore, drinking water resources are spatially separated from the irrigation site, leading to the exclusion of this potential pathway, too.

The pathways of interest are the ones, which lead to direct contact to treated wastewater or wastewater impacted media, like soil particles. Thus, the population groups considered in this paper are people working on the agricultural areas, like farmers and irrigation managers (fieldworker scenario) and people living close to the irrigation site (nearby resident scenario).

As a first step of exposure modeling influent concentrations are estimated. Since no monitoring data are available for microbial parameters exposure assessment has to be based on literature information. Depending on the available information different methods were used to estimate influent concentrations of the selected reference pathogens in the WWTP Steinhof.

4.1 Influent Concentrations

For Norovirus, Rotavirus, Campylobacter and Salmonella estimations are based on available indicator to pathogen ratios. Mara et al. calculated the risk of infection for Norovirus and Rotavirus assuming a ratio of 0.1-1 virus per 10^5 E.coli (Mara et al. 2010). The WHO published the same range for Campylobacter in 2006 (WHO 2006). The estimation for Salmonella concentrations is based on data from Koivunen et al. (Koivunen et al. 2003). A range from 1-100 Salmonella per 10^5 fecal coliforms was derived.

For the influent concentration of indicator organisms a log-normal distribution with a mean (μ) of 7.5 and a standard deviation (σ) of 1 is assumed [1/100 ml]. This corresponds to microbial analysis at the sewage treatment plant in Bad Tölz where influent concentrations of total and fecal coliforms between 10^7 and 10^8 per 100 ml were measured (Huber and Popp 2005). Data published by WHO in 2006, which range from 10^8-10^{10} thermotolerant coliforms per liter, confirm this assumption (WHO 2006).

For Giardia a direct relation between indicator and pathogen could not be found. Instead, data, directly measured in sewage treatment plants in the Netherlands from Medema and Schijven (2001) are taken (Medema and Schijven 2001).

For EHEC no data for wastewater concentrations or relations between EHEC and non-pathogenic E.coli or other indicators could be found. Instead, influent concentrations are based on incidence data of Braunschweig [reported EHEC infections/100000 people].

Using incidence data underreporting has to be considered. Until the outbreak in 2011 laboratories did not analyze the pathogen routinely but just on explicit request of the doctor in charge which makes a reasonable and realistic estimation difficult (RKI, personal correspondence). Therefore, a worst case scenario is applied as a first step. If the scenario leads to an intolerable additional risk of infection the model assumptions will be refined. Otherwise, risk assessment is considered to be finished.

For the worst case scenario incidence values from Denmark, which already include a correction for underreporting, published by Schönning et al. are used (Schönning et al. 2007). They promote a normally distributed incidence (per 100,000 inhabitants) with a mean of 30 (μ) and a standard deviation of 5 (σ). Since, the number of EHEC cases per year gives no information on the distribution of EHEC cases over the year, the maximum number of EHEC bacteria in wastewater can be calculated, by assuming that all the people are infected on the same day.

Assuming an average duration of a EHEC gastroenteritis episode of 8 days (Schönning et al. 2007), this maximum concentration would be present in the sewage treatment plant at 8 days per year. Consequently, on the remaining 357 days the concentration would be zero.

As a worst case scenario the incidence distribution (normal distribution, N (μ, σ), μ=30, σ=5), which refers to the number of cases out of 100,000 inhabitants per year, is used as incidence rate per day.

The number of pathogens excreted by infected people per gram feces is taken from (Schönning et al. 2007). The average amount of feces excreted by humans is taken from (WHO 1992). In order to calculate wastewater concentrations the total number of excreted pathogens is divided by the daily amount of wastewater.

Table 2 summarizes the point estimates and distributions, which were used for the calculation of EHEC concentrations in the influent of the sewage treatment plant Steinhof.

Table 2: Used values for the calculation of influent concentrations of EHEC bacteria. N, LN and Tri refer to the distribution, the values in brackets to the parameters necessary to define them. N (mean, standard deviation), LN (ln(mean), ln(standard deviation)), Tri(min, max, modus)

Factor	Distribution	Parameter/values	Reference
Daily amount of wastewater	Point estimate	57534m³	Abwasserverband Braunschweig
EHEC cases per day	Normal	N (30,5)	Schönning et al. 2007
Pathogens per gram feces	Lognormal	LN (5.8,1.2)	Schönning et al. 2007
Excreted feces per day [g/d]	Triangular	Tri (150,400,300)	(WHO 1992)
PT(Steinhof)	Point estimate	350000 PT	Abwasserverband Braunschweig

4.2 Effluent concentrations

Effluent concentrations are calculated by accounting for pathogen reduction during wastewater treatment. For the reduction of pathogens during wastewater treatment a triangular distribution is assumed (Haas et al. 1999). Minimum and maximum values for pathogen reduction are taken from WHO (2006). The median value to define the triangular distribution is taken from the German Federal Agency for the Environment, Nature Conservation and Nuclear Safety (Umweltbundesamt 2011). The used values are summarized in Table 3.

Table 3: Potential pathogen reduction in log_{10} units for the sewage treatment plant

Treatment step	Distribution	Min [log_{10}]	Max [log_{10}]	Median[log_{10}]
STP	Triangular	0 (Viruses) 1 (Bacteria) 0 (Protozoa)	3 (Viruses) 3 (Bacteria) 2 (Protozoa)	2 (Viruses) 2 (Bacteria) 1.5 (Protozoa)

4.3 Assumptions for exposure scenarios

In two different exposure scenarios the dose of pathogens to which the respective population groups are exposed to via soil/water intake and inhalation is calculated.

4.3.1 Fieldworkers

Field workers (irrigation managers, farmers) are the group most directly exposed to treated wastewater and sewage sludge. An intake of 1-10 mg contaminated soil, or 1-10 µl treated wastewater per exposure event is assumed (Mara et al. 2005 in WHO 2006). No die-off is considered. Soil pathogen concentrations are assumed to equal effluent pathogen concentrations (Number per 100 ml_{water} = Number of 100 g_{soil}). The number of exposure events per year is set to 100 pppy.

4.3.2 Nearby residents

For exposure assessment of nearby residents, the dose of solid and liquid aerosol particles people are exposed to has to be estimated. Viau et al. conducted a QMRA study in 2011, where particle exposure due to biosolid application was modeled. Depending on the wind speed and distance from the site of application they published a range of inhaled PM10 particles from biosolid land application from 0.05 µg per application event at a wind speed of 20 m/s and a distance of 1000 m to 25.3 µg per application event at a wind speed of 1.5 m/s and a distance of 5 m (Viau et al. 2011a).

The legal permission for wastewater reuse in Braunschweig defines minimum distances between the irrigation machine and the landed properties of local residents. Depending on the size of the nozzle outlet of the irrigation machine the minimum distance varies between 60 and 150 m (Weikert 2001). The average wind speed for the region of Braunschweig is set to 3 m/s (DWD 2004). For this wind speed and distance Viau et al. published an inhalation dose of PM10 particles produced by biosolid land application form 4.5-6.9 µg per application event (Viau et al. 2011b). This value is divided by 80 since Viau, Kyle et al. state that “land-applying dewatered biosolids […] produces an aerosol emission rate approximately 80 greater than emission rates observed for liquid sludge spray application” ((Viau et al. 2011b), p.5466, ll. 17-20). The number of exposure events is set to 365, which represent a worst case assumption.

5. Risk characterization

In order to account for uncertainties and variability risk characterization is conducted by the use of Monte Carlo Simulation. The annual probability of infection per person per year (pppy) is calculated in a 1,000 trial simulation. The number of trials for calculating the probability of infection per exposure event depends on the number of exposure events per year.

Fieldworkers are assumed to be exposed 100 days per year. Therefore, 100,000 trials were conducted. The 100,000 trials are grouped in groups of 100 (number of exposure events per year), resulting in 1000 trials for the total annual risk. This approach follows the improved procedure of Monte Carlo Simulations for wastewater irrigation elaborated by Karavarsamis and Hamilton in 2009, published in Drechsel et al. (2010). The number of exposure events for nearby residents is set to 365 days, which represents a worst-case assumption.

The calculated probability of infection is multiplied by the pathogen-specific disease per infection ratio and the specific severity factors for DALY calculation. Results are presented in Figure 3 and Figure 4.

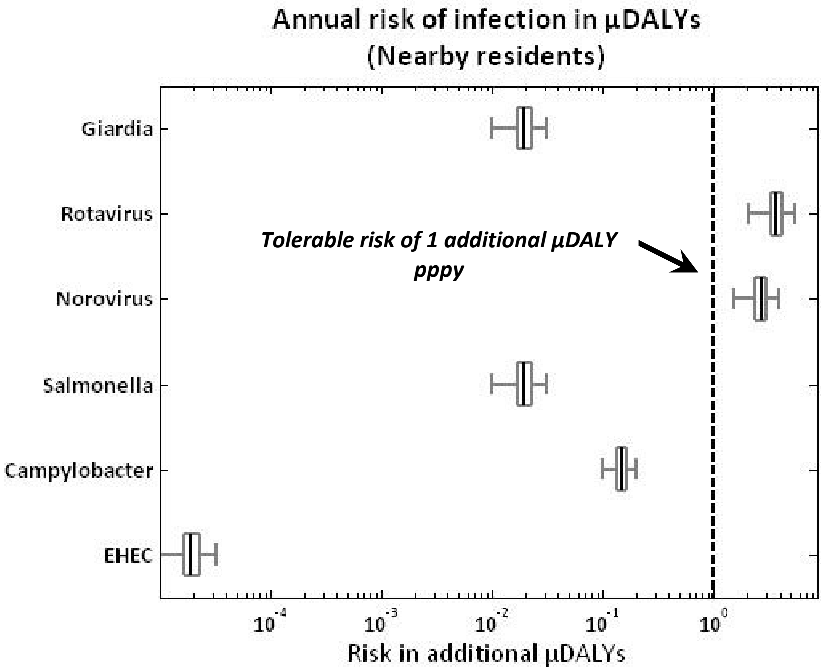


Figure 3: Annual risk per person per year expressed in µDALYs for nearby residents. The black line represents the median of the respective distribution, the edges of the boxes the respective 25 and 75-percentiles, the grey line the remaining values. The dotted black line represents the level of tolerable risk set by the WHO wastewater guidelines

Against the background of made assumptions the risk for nearby residents due to bacterial and protozoan pathogens is at least one order of magnitude below the tolerable level. Although based on drastic worst-case assumptions the risk of EHEC exposure is about five orders of magnitude below the tolerable level. Finally, for the risk of viral infections the value of 1 µDALY is slightly exceeded. However, since pathogen die-off is not considered and the number of exposure events is set to 365 the model has to be refined in order to make a final statement concerning the risk of viral infection.

For fieldworkers the results for Giardia Salmonella and Campylobacter show the same picture as viruses in the residents-scenario. Again, due to the made assumptions the results cannot be regarded as a significant exceeding of the tolerable value. In contrast, the risk of viral infections clearly exceeds the tolerable value. The risk of EHEC infection lies about four orders of magnitude below the tolerable level.

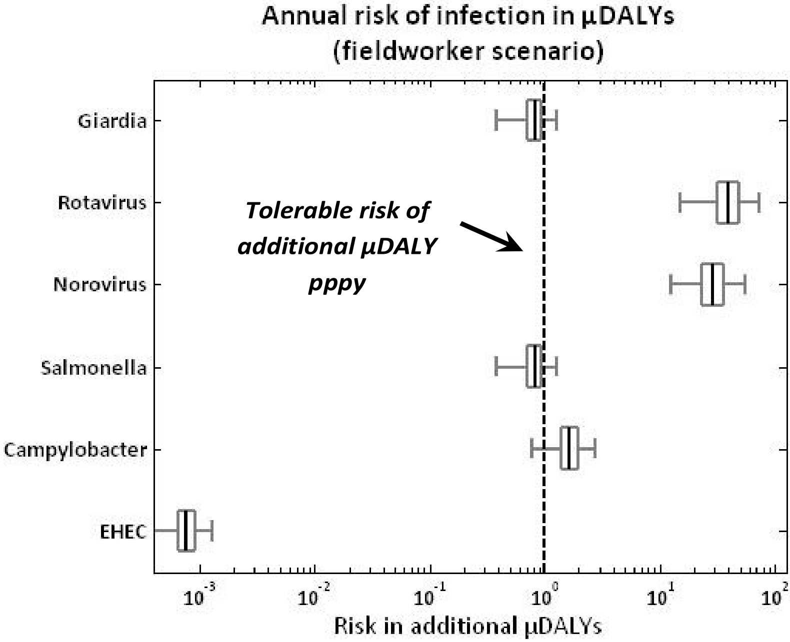


Figure 4: Annual risk per person per year expressed in additional µDALYs for fieldworkers. The black line represents the median of the respective distribution, the edges of the boxes the respective 25 and 75-percentiles, the grey line the remaining values. The dotted black line represents the level of tolerable risk set by the WHO wastewater guidelines

6. Conclusions

The study presented one way to cope with the problem and health risk assessment related to agricultural water reuse. On the one hand, since calculations for pathogens are solely based on literature values the result must not be seen as an assessment of the “safety” of the reuse scheme in Braunschweig but rather presents a way of quantifying uncertainties. On the other hand the conducted QMRA clearly supports priority setting, thus, supporting the implementation of a more risk-based management approach. Viral infections can clearly regarded as being “of concern” for people working on the agricultural areas in BS, whereas EHEC can be considered as not, neither for fieldworkers nor for nearby residents. In order to be in compliance the current WHO limit value an additional pathogen removal of 1.5 log units would be necessary.

Acknowledgements

Veolia Water and Berliner Wasserbetriebe are gratefully acknowledged for the funding of CoDiGreen. Finally, all colleagues in Braunschweig are thanked for their valuable input and discussions which contributed to the success of this study.

References

Alan D. Lopez, C. D. M., Majid Ezzati, Dean T. Jamison, Christopher J. L. Murray, Ed. (2006). Global Burden of Disease and Risk Factors. Washington DC, Oxford University press, The World Bank.

Asano, Leong, et al. (1992). "Evaluation of the California Wastewater reclamation criteria using enteric virus monitoring data." Water Science and Technology 26(7-8): 1513-1524.

Caroline Schönning, Therese Westrell, et al. (2007). "Microbial risk assessment of local handling and use of human faeces." Journal of water and health 05(1): 117-128.

Drechsel, P., C. Scott, et al., Eds. (2010). Wastewater irrigation and health-Assessing and Mitigating Risk in Low-Income Countries. London, Sterling VA, International Development Research Center, Earthscan.

DWD (2004). Jahresmittel der Windgeschwindigkeit - 10m über dem Grund- in der Bundesrepublik Deutschland. Offenbach, Deutscher Wetterdienst, Abteilung Klima- und Umweltberatung: Statistisches Windfeldmodel, Bezugszeitraum 1981-2000.

Eggers, T. (2008). "Verregnung von geklärtemAbwasser auf 3000ha langwirtschaftlich genutzten Flächen." Wasser(Abwasser 149(13).

Fewtrell, L. and J. Bartram, Eds. (2001). Water Quality, Assessment of risk and risk management for water-related infectious disease, IWA Publishing, SMITTSKYDDSINSTITUTET, World Health Organization.

Haas, C. N., J. B. Rose, et al. (1999). Quantitative Microbial Risk Assessment, John Wiley & Sons, Inc.

Hamilton, A. J., Stagnitti, et al. (2006). "Quantitative Microbial Risk Assessment, Models for Consumption of raw vegetables irrigated withi reclaimed water." Applied and Environmental Microbiology 72(5): 3284-3290.

Henning, K. J., D. J. Bräunig, et al., Eds. (2010). Leitfaden für gesundheitliche Bewertungen. Rostock.

Huber, S. and W. Popp (2005). Überprüfung der Abtötung bzw. Inaktivierung ausgewählter Krankheitserreger in Abwasser durch UV-Strahlung im Vergleich zur Reduktion von Fäkalindikatorbakterien und Untersuchungen zur Wiederverkeimung, Bayerisches Landesamt für Umwelt.

Koivunen, J., A. Siitonen, et al. (2003). "Elimination of enteric bacteria in biological-chemical treatment and tertiary filtration." Water research 37: 690-698.

Mara, D., Blumenthal, et al. (2007). "Health risks in wastewater irrigation: Comparing estimates from quantitative microbial risk analyses and epidemiological studies." Journal of water and health 05(1): 39-50.

Mara, D., C. Hamilton, et al. (2010). WSHH Guidance note 4, More appropriate tolerable additional burdenof disease, Improved determination of annual risks, Norovirus and Ascaris infection risks, Extended health protection control measures,Treatment and non-treatment options. OMS-WSHH-Guidance note, World Health Organisation.

Mara, D. and A. Sleigh (2010). "Estimation of norovirus infection risks to consumers of wastewater-irrigated food crops eaten raw." Journal of water and health 08(1): 39-43.

Medema, G. J. and J. F. Schijven (2001). "Modelling the sewage discharge and dispersion of Cryptosporidium and Giardia in surface water." Water research 35(18): 4307-4316.

Ripke, H. Nutzung alternativer Wasserresourcen für die Zusatzbewässerung, Abwasserverband Braunschweig.

Robert-Koch-Institut (2011). SurvStat, http://www3.rki.de/SurvStat, deadline: 09.08.2011.

Rose, J. B., C. N. Haas, et al. (1991). "Risk Assessment and Control of Waterborne Giardiasis." American Journal of Public Health 81(6).

Salgot, Huertas, et al. (2004). "Wastewater reuse and risk:definition of key objectives." Desalination 187: 29-40.

Teunis, F. M., C. L. Moe, et al. (2008). "Norwalk Virus: How infectious is it?" Journal of Medical Virology 80: 1468-1476.

Umweltbundesamt (2011). FAQ EHEC. Umweltbundesamt. Dessau-Roßlau.

Viau, E., B. Kyle, et al. (2011a). "Supporting information of "Toward a consensus view on the infecious risks associated with land applying sewage sludge" " Environmental Science and Technology 45.

Viau, E., B. Kyle, et al. (2011b). "Toward a consensus view of the infectious risks associated with land application of sewage sludge." Environmental Science and Technology 45: 5459-5469.

Weikert, W. (2001). Wasserrechtliche Erlaubnisse; Änderungen der Erlaubnis zur Beregnung mit bahandeltem Abwasser aus dem Klärwerk Braunschweig für den Abwasserverband Braunschweig. 2399/01. B. Braunschweig.

Westrell, Schönning, et al. (2004). "QMRA (quantitative microbial risk assessment) and HACCP (hazard analysis and critical control points) for management of pathogens in wastewater and sewage sludge treatment and reuse "Water Science and Technology 50(2): 23-30.

WHO (1992). "A guide to the development of off-site sanitation."

WHO (2006). Guidelines for the safe use of wastewater, excreta and greywater, World Health Organization. Volume 2.

Author

Wolfgang Seis

Berlin Centre of Competence for Water

Cicerostr 24

10709 Berlin, Germany

Tel.: +49 30 53653 807

Fax: +49 30 53653 888

wolfgang.seis@kompetenz-wasser.de

www.kompetenz-wasser.de

The Braunschweig Model

Utilisation of cleared wastewater in agriculture for the purpose of preserving ground water reservoirs

Bernhard Teiser

Managing Director of the Wastewater Board Braunschweig

Summary

The Wastewater Board Braunschweig was founded in 1954 as a water and soil association in accordance with the provisions of the Water Association Act. The members of this public body are

- the City of Braunschweig and
- the Gifhorn Water Board as a supplier of wastewater and
- the owners of the properties used as agricultural areas who act as recipients of the wastewater.

The association's responsibility is to irrigate approx. 2,700 hectares of agricultural production area with wastewater and utilise both the water and the nutrient matter it contains in a useful manner. This agricultural wastewater reuse translates to

- lower fees for the consumer thanks to the reduced costs involved in expanding and operating the wastewater treatment plant,
- permanently secure and high yields thanks to the efficient utilisation of water and nutrients in agriculture
- the preservation of groundwater resources thanks to the use of wastewater for irrigation.

Image 1: Map of the association's territory

1. Introduction

Even though there is no shortage of water in Germany, certain areas of the country experience water scarcity during extended periods of dry weather. The water industry discovered the solution to this problem decades ago when they decided to transport water from surplus areas to areas in need of water using long-distance water lines. An example of this solution is the supply of cities and communities in Northern Germany with water originating from the hydro dams found in the Harz region.

This solution is, however, not an option when it comes to irrigating large surfaces that are used to cultivate plants. Apart from the fact that the necessary irrigation fluctuates from one year to the next on account of the climatic conditions, plants require irrigation for their growth only during a certain period.

Generally speaking, Germany's annual climatic water balance is positive as precipitation exceeds evaporation. Unfortunately, this statement does not apply to the growing season of plants. As weather records show, the periods showing a negative water balance in the North-Eastern part of Lower Saxony, the region of Germany with the highest rain quantities, have been on the increase for decades. The farmers in said region, which also includes the Lüneburg Heath, use the light soils with index numbers ranging between 18 and 35 for intensive agriculture. For the reasons specified above, the shortage in precipitation found in this region, needs to be offset by irrigation.

According to a ban that is in place in Lower Saxony, extracting water from the "flowing wave" of rivers and lakes is prohibited. This leaves the extraction of groundwater, which, however, is restricted by law in order to ensure that the receiving waters do not dry out and to prevent the ecological system of the wetlands from being affected.

The restrictions are enforced by water extraction permits which allow for the extraction of volumes that average 80 mm per hectare and year over a period of seven years. Given the present conditions, these strictly limited quantities of water would not suffice to irrigate the fields cultivated by the Wastewater Board Braunschweig. The only way to solve this problem was to exploit the wastewater produced in the City of Braunschweig.

2. Wastewater reuse in Braunschweig

Braunschweig can look back on a tradition of wastewater reuse in agriculture that spans over one hundred years.

The infiltration fields, which are still used to date, were put into service in 1895. They were utilized in agriculture for cultivating vegetables until 1962, when they were converted to play a part in the biological post-treatment of sewage processed in the wastewater treatment plant. They also serve as a resting and breeding ground for a large variety of different birds. Designed to serve only 100,000 residents the infiltration fields became too small to absorb the growing population even before World War II was over. Instead of expanding the infiltration fields or constructing a wastewater treatment plant, the city decided to plan a wastewater irrigation system. To this end, the Wastewater Board Braunschweig was established in 1954 as a soil and water association. The association completed the development of four pumping station districts including 2,700 hectares of irrigation land on an area extending over 4,000 hectares after four stages of construction. The expansion involved the installation of 100 kilometres of underground lines including 900 subsurface hydrants which are used to extract the water for the sprinkling machines.

3. Requirements for agricultural wastewater reuse

Wastewater reuse all year round is only possible in places that meet the necessary requirements. The climate as well as the quality of the soil found in Germany limit the need for irrigation to a small number of areas. This is also the main reason why wastewater reuse in agriculture is not common practice in Germany and the construction of large-scale installations ended with the facilities in Braunschweig and Wolfsburg.

Climatic data gathered by the German Weather Service at the Braunschweig weather station reveals that the climatic weather balance of the region was negative between the months of April and September. The deficit at the time the association was founded amounted to 122 mm. The average shortage experienced during the growing season swelled to 181 mm over the last ten years. The drop in precipitation in the spring and the summer is largely offset by greater precipitation during the winter time, which might be attributable to the evident rise in the average annual temperature.

Wastewater application all year round requires light soils in level terrain. The light soils are capable of absorbing additional water even after previous precipitation. The level terrain is necessary to allow the water to evenly distribute itself across the surface without running off or coalescing. This second most important requirement is satisfied in Braunschweig.

If necessary, groundwater levels of approx. 1.50 metres beneath the surface must be created by drainages that need to be laid at a corresponding depth.

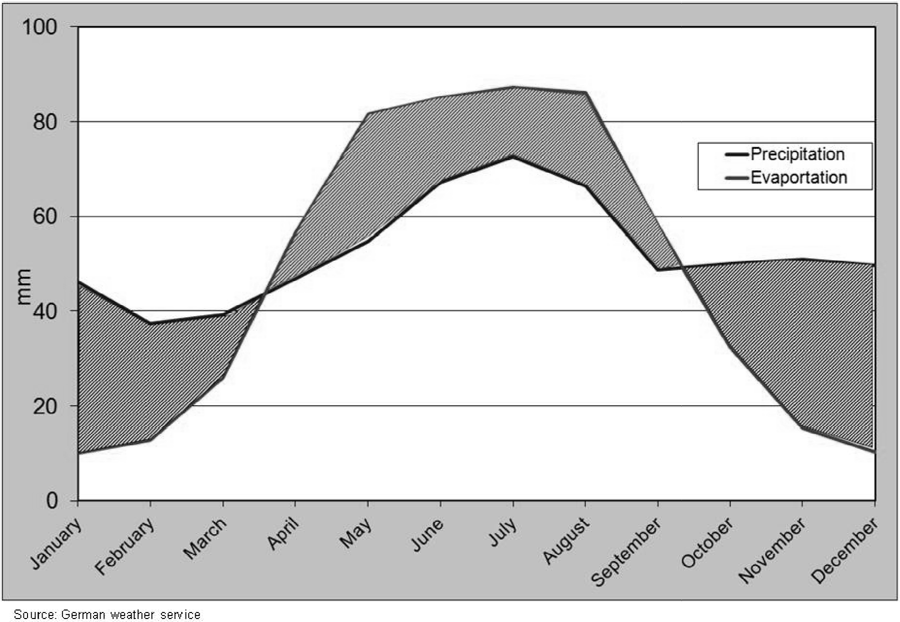


Image 2: Average climatic water balance between 1921 and 2011

A population density that is as low as possible is desirable in light of the fact that the "water extraction permits" granted by the water authority - especially with regard to the safety distances that need to be observed to public waterways, etc. - may result in restrictions that are unacceptable from an economic standpoint. Another factor that needs to be taken into account is the acceptance shown by the local residents. The level of acceptance can only be increased by suitable measures geared towards the elimination of offensive odours.

The use of modern irrigation equipment and machinery and, thus, the economically advantageous application of irrigation are, ultimately, dependent on perfect size and shape of the fields. The people in charge in Braunschweig satisfied this requirement with a reallocation and consolidation plan that led to the creation of a network of roads and waterways and a corresponding network of underground lines and extraction hydrants.

4. Benefits of agricultural wastewater reuse

The consultations preceding the establishment of the association naturally revolved around the benefits as perceived by all parties involved.

The City of Braunschweig was able to scrap the need for building and operating a wastewater treatment plant.

While a wastewater treatment sewage plant was built in the meantime and diminished the former advantage of the wastewater supplier (raw wastewater irrigation), the modified wastewater treatment plant expansion (lower capacities of the secondary settling basins, no filtration, etc.) represents a clear advantage for wastewater irrigation over the conventional operation of a wastewater treatment plant. The irrigation with fermented sludge, which is now possible as well, must be deemed another advantage both to the wastewater supplier (reduced waste management costs) and the farmer (nutrient matter).

The most significant aspect for agricultural businesses, however, is the utilisation of the ingredients as well as the fertilising and organic matter contained in wastewater and, first and foremost, the supply of the water. Apart from enhancing light sandy soils by adding organic matter and increasing their ability to retain water, irrigation replenishes nutrients, counteracts the average decrease in precipitation that was observed in recent years during the growing season and offsets the climatic water balance.

The nutrient quantities applied with the wastewater every year amount to

- 67 kg/ha in mineral nitrogen,
- 80 kg/ha in P_2O_5,
- 90 kg/ha in K_2O,
- and sulphur and lime in significant quantities.

Wastewater/sewage sludge is capable of supplying almost the entire fertilisation with phosphorus.

The supply of the missing water produced the desired and expected increase in yields. More importantly, wastewater reuse makes it possible to cultivate different kinds of more demanding fruits (sugar beets, corn, wheat, etc). In this regard, it is difficult to overestimate the role irrigation plays in securing crop yields as it, from a business management standpoint, assures the liquidity and the existence of the businesses over the long term. Another aspect that needs to be mentioned in this regard is contracted cultivation, which today is a common phenomenon in many areas of agriculture. This type of cultivation and the associated obligation to fulfil a contract would be unfeasible on the light soils found in the region.

From today's viewpoint, another advantage is linked to the aspects of ecology, environmental protection and circular economy. The following needs to be mentioned in this regard:

- The protection of the receiving water against residual contamination. After all, the use of wastewater reuse made it possible to enhance the water quality in the Lower Oker north of Braunschweig to quality grade II (moderately contaminated).
- Supply with irrigation water from wastewater instead of groundwater. Supplying the water that is necessary on average to irrigate the fields operated by the association would require 4 - 5 million m^3 of groundwater a year.
- The above-mentioned dual use of the water as well as the utilisation of the ingredients and the sewage sludge in terms of the circular economy legislation that is authoritative today.

Image 3: Sprinkling machine

The pipe irrigation method, which was initially applied during the first decade of use irrigation, required a great amount of manpower, especially during the main irrigation season. In an effort to reduce this need, the association developed sprinkling machines. This irrigation technique was later to become the field irrigation method most commonly applied in the Federal Republic of Germany.

5. Challenges

One of the problems that jeopardised the survival of wastewater irrigation were the offensive odours caused by the raw sewage that farmers used to dispense in the first 20 years and which was only subjected to mechanical cleaning. The locals residing in or close to the irrigation area were no longer willing to accept the unpleasant odour. All investigations and attempts undertaken to remedy this nuisance ultimately resulted in the construction of a pre-treatment plant, i.e. a wastewater treatment plant including biological cleaning stage, which was used to merely mineralise and degrade the organic matter that had just begun to decay. The proposal was turned into reality in 1979, resulting in the first of several stages of construction required to expand the Steinhof wastewater treatment plant. Fortunately, the project met with the expected success.

Image 4: Steinhof wastewater treatment plant

The tolerable values measured in the soil and the sewage sludge as specified in the sewage sludge ordinance could not hide the fact that action was needed in order to prevent contaminants from accumulating over extended periods of time. Starting in 1980, inspections at the dischargers were performed by the channel network operators and resulted, for instance, in cadmium load reduction in excess of 90%. In 1985, the amendment to the Federal Water Act provided for the option to charge severe fines for violations against the city's wastewater ordinance that had been revised accordingly.

The measures resulted in contaminant levels that fell both below the limits defined in 1982 and the significantly tightened limits set forth in the sewage sludge ordinance in 1992. A side effect of the unexpected success brought about by the discharger inspections conducted in approx. 500 businesses was the economically feasible use of sewage sludge in agriculture.

Nitrogen, one of the vital nutrients promoting growth in plants, is contained in wastewater. The permeability of the light sandy soils suggests that the easily soluble nitrate is washed out, allowing it to enter the groundwater. We, furthermore, assume that this process is intensified during the application of the wastewater as it takes place all year round and largely regardless of the natural weather conditions. For the reasons mentioned above, public agencies constantly examine groundwater and drainage samples taken in the irrigation area. They show that the contamination levels are not as high as one might expect.

Over the years, the association has taken a great number of measures intended to counteract the displacement of nitrate - without being coerced to do so by statutory regulations or requirements. The most important measures during the period of low vegetation:

- The elimination of more than 90% of nitrogen by means of nitrification and denitrification in the wastewater treatment plant.
- The reduction of the applied wastewater volume thanks to measures ranging from the intensive usage of the restructured infiltration fields to the suspended irrigation in the winter time.
- The promotion of winter tillage cultivation for the purpose of green manuring as well as the absorption and fixation of the residual nitrate that is not utilised by the plants.
- The consultation of the farmers regarding the existing minimum nitrogen values.
- Week-long instructions of the farmers about the nutrients contained in the applied wastewater. These instructions allowed the farmers, first and foremost, to include the mineralised nitrogen, which can be absorbed by the plants, in their fertilisers.
- The establishment of a land register related to field size in accordance with the provisions of the fertilisation ordinance.
- The briefing of the farmers about all important questions and problems at the annual meetings prior to the commencement of the work in the spring.

Finally, mention has to be made of the poorly degradable organic contaminants, which have attained increasing attention over the last few years. The sewage sludge ordinance of 1992 acknowledges this increased importance by requiring analyses intended to determine the halogenated hydrocarbons subsumed under sum parameter AOX as well as dioxins and furans. The findings of the investigations conducted in Braunschweig provide no reason to assume that the prescribed limits might be reached or even exceeded at some point.

Microcontaminants such as pharmaceutical residues, fragrances and other poorly degradable contaminants, which have now come under increased scrutiny, are eliminated to a greater extent by the passage through the soil than the discharge into a body of water. This fact has been proven by the European research project "Poseidon".

6. The Braunschweig wastewater concept

A concept devised for Braunschweig and the affiliated communities with a total number of inhabitants and population equivalents equal to 350,000 was developed many years ago and provides for

- the cleaning and supply of the entire wastewater purified in the Steinhof wastewater treatment plant - approx. 20 million m^3/a - for the purpose of irrigating agricultural crop land or secondary treatment on the infiltration fields,
- the prevention of purified wastewater from being discharged from the wastewater treatment plant directly into the River Oker.

This concept has effected the continuous improvement of the water quality in the Oker that has been mentioned above. This is an unprecedented result for Lower Saxony and, quite possibly, other regions as well!

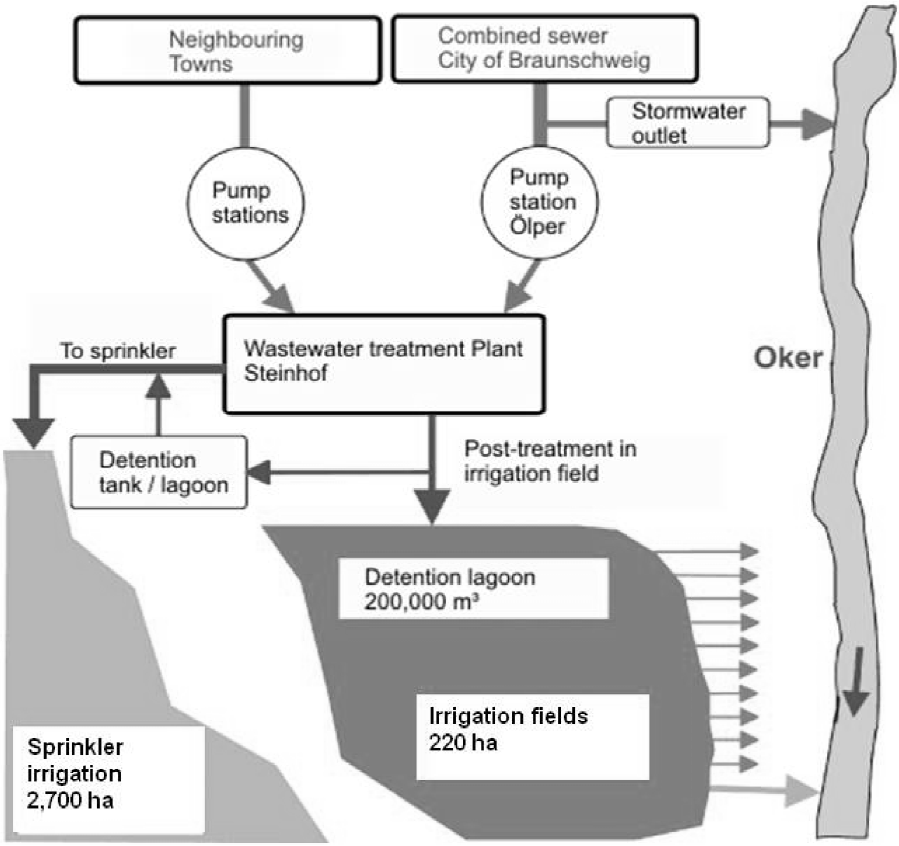


Image 5: Braunschweig wastewater concept

7. Renewable resources

To present farmers with the option to fall back on renewable resources if experiencing difficulty with their food production, the association erected a biogas plant in the irrigation area which generates 2.5 MWel of biogas. 80% of the gas is transported directly to Braunschweig via a 20 km pipeline, where it is converted into electricity and, finally, fed into the municipal networks as electricity and heat. We have named this circle of water, nutrients and energy "The Braunschweig Model".

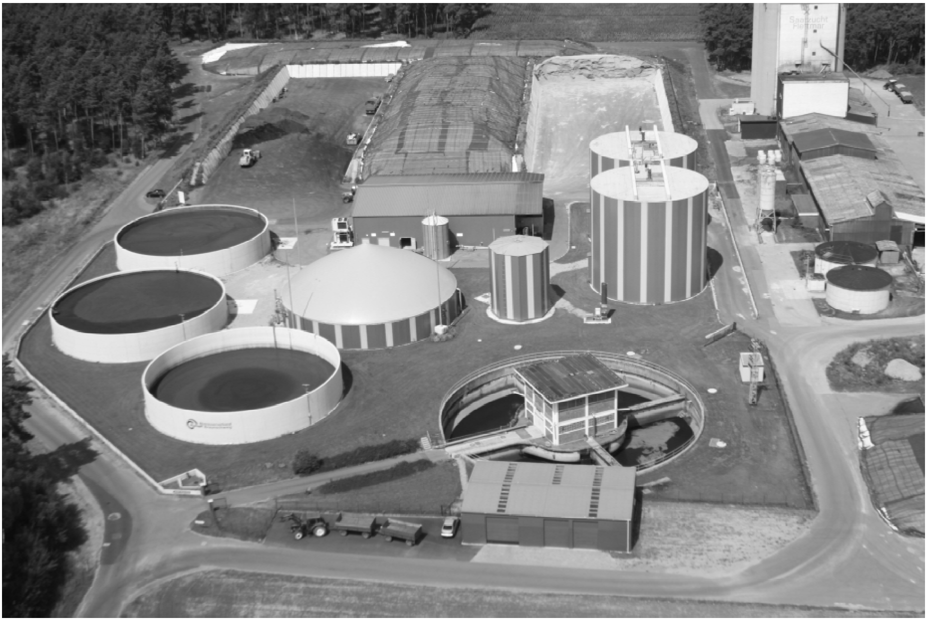


Image 6: Hillerse biogas plant

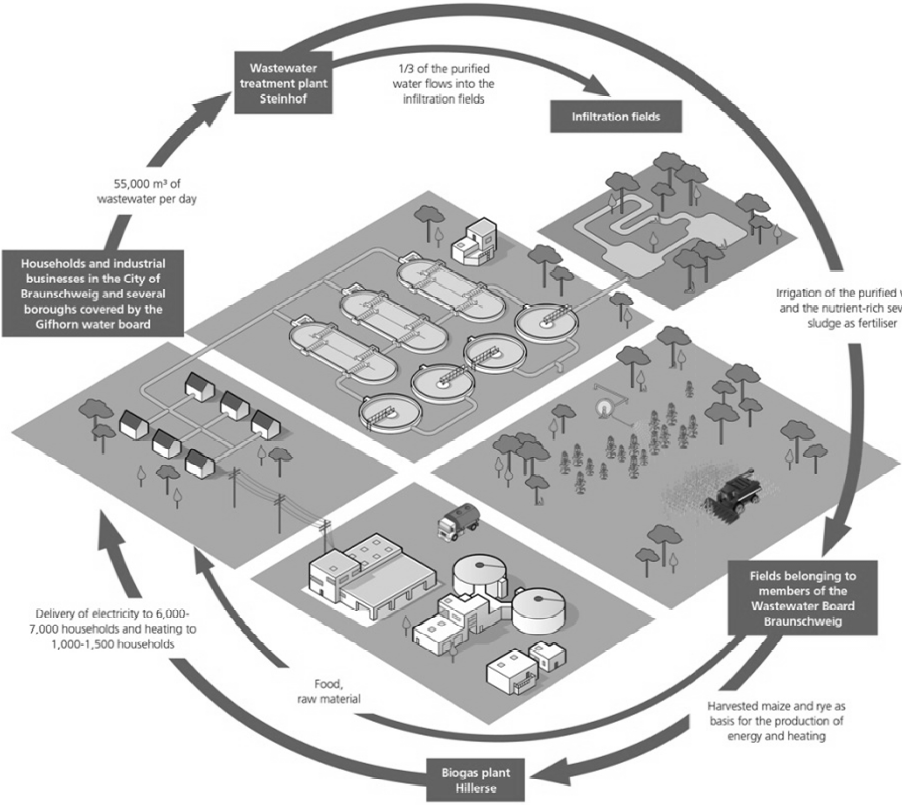


Image 7: The Braunschweig Model

8. Outlook

Land treatment of wastewater is the oldest form of wastewater reclamation. However, this close-to-nature method is used and developed only in a few number of cases.

The Wastewater Board Braunschweig has maintained and expanded this system. The efforts taken by the association managed to solve many problems and overcome much opposition.

The system the association developed provides a contemporary and ground-breaking approach, especially in light of the fact that groundwater resources that can be used by agriculture are becoming increasingly scarce, that the world's phosphate reserves are finite and that the reduction of contaminants critical.

The association will continue to promote the agricultural utilisation of sewage sludge and wastewater – today and in the future!

Author

Bernhard Teiser

Geschäftsführer

Abwasserverband Braunschweig

Celler Straße 22

38176 Wendeburg

Non-potable water reuse for landscape irrigation in Berlin, Germany

F. Wode, R. Gnirss*, U. Duennbier*, K. Moeller **, F. Hecht***, T. Taute****

**Berliner Wasserbetriebe **Umweltvorhaben Dr. Klaus Möller GmbH, Berlin ***Freie Universität Berlin*

Abstract

Berliner Wasserbetriebe provides safe drinking water and treats wastewater for the 3.4 million inhabitants of Berlin, one of the most populous urban areas in Europe. The treatment of drinking water in Berlin mainly consists of bank filtration and artificial recharge (via infiltration ponds). Berlin's water cycle is partially closed, which represents a challenge for sustainable water management. In order to reduce the pollution of surface waters and release the pressure on the urban water cycle, a non-potable reuse of treated wastewater for landscape irrigation is currently investigated in the R&D project ELaN, funded by the German Ministry of Education and Research (BMBF). For this research, a limited permit was given to apply approximately 5000-10.000 m³/day of secondary effluent from the wastewater treatment plant Schoenerlinde on irrigation fields for further treatment. The reclaimed water use was found to have multiple benefits. A conservation of the wetland ecosystem and wildlife habitat was ensured. Moreover, the polishing ponds showed a potential for reduction of pathogens and nitrogen and degradation of some trace organic compounds (TrOCs). Surface water passage resulted in a further concentration decrease by dilution. An impact on a receiving river was determined, manifesting in increased TrOC and nutrient concentrations. Still, compared to a direct discharge the reclaimed water use was found to be more favourable.

1. Introduction

According to the World Bank, "The greatest challenge in the water and sanitation sector over the next two decades will be the implementation of low cost sewage treatment that will at the same time permit selective reuse of treated effluents for agricultural and industrial purposes" (Looker, 1998). It is crucial that sanitation systems have high levels of hygienic standards in order to prevent the spread of diseases. Other treatment goals include the recovery of nutrient and water resources for reuse in agricultural production as well as the reduction in the overall (user)-demand for water resources (Rose & International Development Research, 1996).

Berliner Wasserbetriebe (BWB) provides safe drinking water and treats wastewater for the 3.4 million inhabitants of Berlin, one of the most populous urban areas in Europe. The objective pursued by the Berlin Senate and BWB is to adapt a management strategy which allows the city to rely on its own water resources. The treatment of drinking water in Berlin mainly relies on bank filtration and artificial recharge (via infiltration ponds). In summer, the minimum flow rates (MNQ) of the river Spree is 2.3 m^3/s in average, for Havel and Dahme the average MNQ are in the same order of magnitude (Möller&Burgschweiger, 2008). The wastewater discharge from Berlin's six treatment plants is also in this order of magnitude. Therefore, the Berlin water cycle is partially closed, which represents a challenge for sustainable water management (Heberer et al., 2004, Massmann et al., 2004). German (European) law only allows wastewater reuse on a case to case basis. Examples are Braunschweig, where advanced treated wastewater is used for agricultural purposes. The aims are nutrient recycling, cultivation of energy crops and advanced treatment of the treated wastewater. Another example in Germany is Wolfsburg, where treated wastwater is used for cultivation of energy crops and groundwater recharge. Studies show that trace organics and pathogens can be removed in the subsurface. Nevertheless, pharmaceuticals such as phenazone and carbamazepine (annual consumption up to 170 t and 88 t per year (Huschek, 2005) can still be found in the effluent of treated wastewater. Both compounds are polar, which allows them to pass barriers in the water cycle such as wastewater treatment plants or bank filtration. Carbamazepine is persistent and can be used as wastewater tracer (Scheurer et al., 2011).

1.1 Aims of the Project

In order to reduce the pollution of surface waters and to release the pressure on the urban water cycle, a non-potable reuse of treated wastewater for landscape irrigation is currently investigated by the R&D project ELaN, funded by the German Ministry of Education and Research (BMBF) (Gnirss et al., 2011). Secondary effluent will be polished by infiltration via polishing ponds on former irrigation fields to remove nutrients, bacteria, viruses and trace organics. The goal is to generate a value for recreation, renewable energy, farmland and wild animal wetland for this heavily modified ecosystem without mobilizing nutrients, heavy metals and trace organic compounds (TrOC). Potential chemical and ecotoxicological risks associated with wastewater reuse will be identified. Based on the scientific assessment the R&D project ELaN aims towards sustainable water reuse and land management written as a decision tool taking into consideration technical, economic, ecological, social and administrative aspects and including all relevant stakeholders in the case study. The use of treated wastewater in the landscape will also help minimize the impacts of climate change by buffering extreme weather conditions (Droughts, Flooding).

2. Materials and methods

2.1 Study site

The site of this study is the catchment area of the Lietzengraben in the north of Berlin with an area of approx. 54 km². This trench system connects several ponds and is mainly fed by drainage water from irrigation fields, which had been used for more than 80 years to treat the raw sewage of the city with only mechanical pretreatment. The infiltration rate in the beginning was estimated with 6.2 mm/d but increased to up to 22 mm/d in the last twenty years of operation. Due to a high input of nutrients, heavy metals and trace organics, the soil structure is heavily disturbed and the production of food crops is no longer allowed. After 1985, when irrigation with raw sewage was stopped, forestation of the area was attempted, but not fully successful due to declining groundwater levels and water scarcity. Later, clay was introduced in the upper soil layer to prevent pollutant emissions into the groundwater. The hydrogeological structure consists of three sandy aquifers, which are separated by confining layers (glacial drift). The surficial, unconfined aquifer is influenced by irrigation water, whereas the two principal, confined aquifers below are assumed to not be influenced by the reused water. A detailed hydrogeological description can be found in (Thierbach et al., 1998). For this research, a limited permit was given to apply approximately 5,000-10,000 m³/day of secondary effluent from the wastewater treatment plant (WWTP) Schoenerlinde on the irrigation fields to restore the ecological status and to study polishing ponds in regard to post treatment. Figure 1 shows a map of the study site and sampling points for ground, drainage and surface water. The travel time in the surface water is estimated with approximately 2 days.

2.2 Sampling campaigns

From 2004–2013, temperature, precipitation, surface water levels and flow have been continuously measured. Since start of the R&D project ELaN in 2011, monthly surface water monitoring from March-October was performed. Examined parameters were nutrients, sulphate, chloride, heavy metals, total organic carbon (TOC) and trace organic compounds (TrOC). In addition, to evaluate the microbial contamination, Escherichia Coli and Enterococcus were determined in September 2013 in surface water. A groundwater monitoring for nutrients, heavy metals and TrOC was performed quarterly, the results are not discussed here.

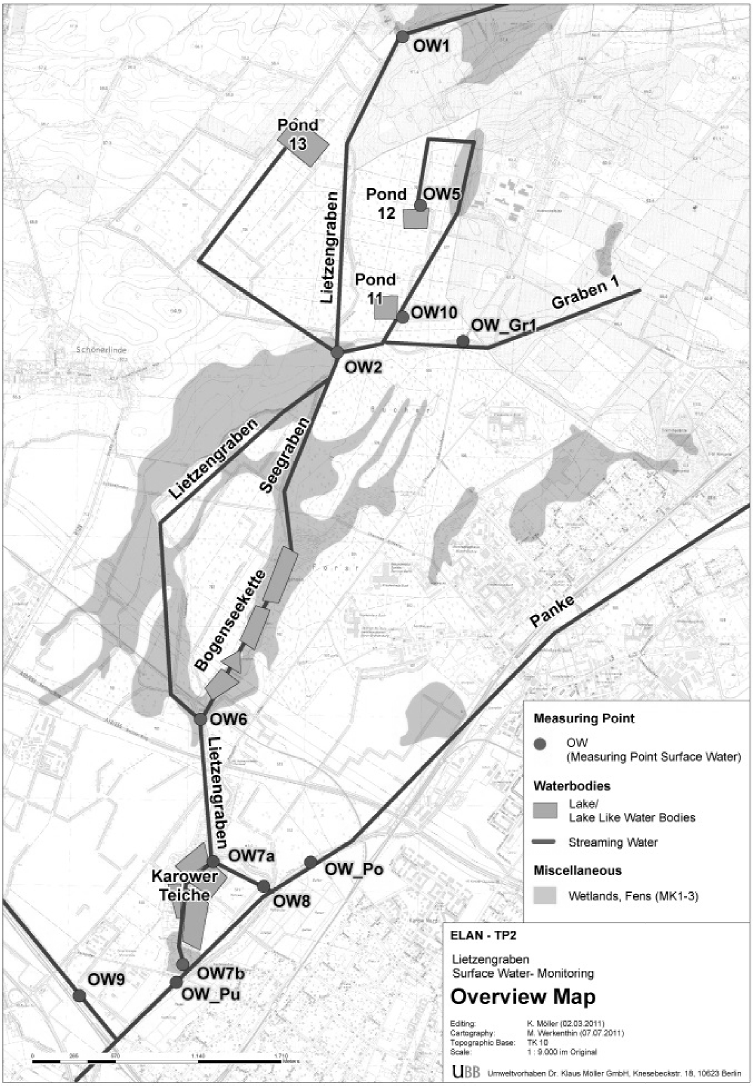


Figure 1: Project area Hobrechtsfelde-Berlin, situated on former irrigation fields

2.3 Analysis of Trace Organic Compounds (TrOC)

Ultra high performance liquid chromatography coupled with high resolution mass spectrometry (UHPLC-HRMS) using an Exactive Plus (Thermos Fischer Scientific) was used for the determination of TrOC. The method is described in detail in (Wode et al., 2012).

3. Results and discussion

3.1 Hydrology

After 1985 the irrigation fields were not receiving any additional water because WWTP Schoenerlinde had been built and started operation. The effect on the hydrology of the area was tremendous, e.g. the through flow of the surface water diminished and water table dropped by 0.5 – 2 m. Detailed analysis of hydrogeological and quality measurement campaigns from the period 1990-1995 are given in (Ginzel et al., 1995) and will be the base line to compare the effect of studies conducted to stabilize the irrigation field as an ecosystem for animals by receiving treated effluent water of the WWTP. Since 2005, advanced treated effluent has been discharged into the irrigation fields with a flow rate of about 5,000 m^3 / day (55 L/sec). Infiltration into groundwater is assumed to be restricted by a thick layer of clay and the infiltration rate was estimated to be 3-5 L/s (annual average) for each irrigation pond.

In Figure 2, rain events are shown in relation to the flow rate at sampling spots OW 1, OW 2 and OW 6 from 2011 to 2012. Seasonal variations and varying weather conditions result in OW6 in flow rates between 30 L/s in summer (August 2012) and up to 600 L/s after a heavy rain event (July 2011). The discharge of the advanced treated water in the irrigation field ensured a steady flow into the landscape. Although a constant flow of WWTP effluent was applied, there were significant monthly variations in water flow in the Lietzengraben as well as in the receiving river Panke due to weather conditions. The ecosystem Lietzengraben, which has a high population of water birds and plants, would be regularly dry without additional water, leading to a destruction of habitats and probably a loss in biodiversity.

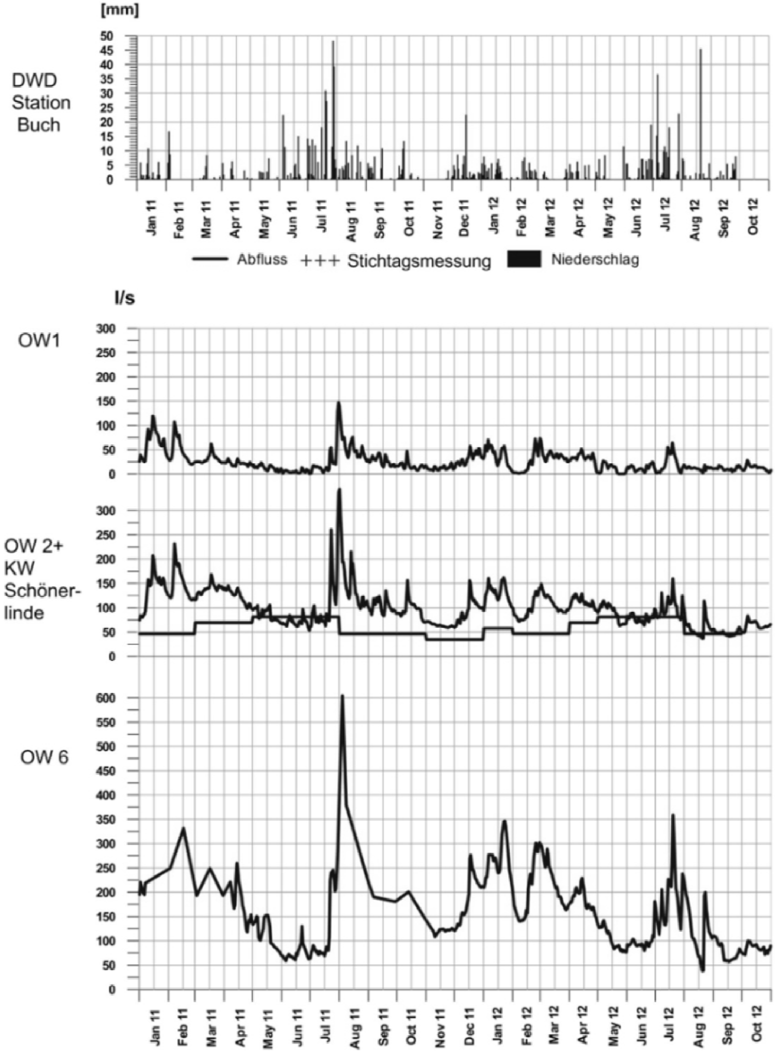


Figure 2: Precipitation and flow rate at different surface water sampling spots for 2011-2012

As shown in Figure 3, after start of the irrigation with treated wastewater (WWTP effluent, 58 L/s), the groundwater table could be stabilized at an average value of 54.5 m NHN (BU 32). Annual variations due to precipitation patterns and seasonal changes had still a strong impact of more than 0.5 m.

Figure 3: Groundwater table in the irrigation field from 2004 to 2013

3.2 Comparison of historic and present contaminant loads in the applied wastewater

Over a period of more than 80 years raw sewage has been discharged onto irrigation fields, resulting in a high inventory of nutrient, heavy metals and organic compounds. Heavy metal accumulations in the soil were characterized by a large spatial variability, but reaching high concentrations of Cd, Cu and Zn (Marschner & Hoffmann, 2000). In the frame of the R&D project ELaN, the inventory of nutrients and organic compounds was focussed. Mean concentrations of raw sewage in relation to secondary effluent from WWTP Schoenerlinde (analysed every second day as 24-hour mixed samples) and irrigation ponds effluent is shown in Table 1. Over the years influent concentration and load for COD and ammonium per capita was very constant, only phosphorus is about 20% lower due to substitution of detergents. Since 1990, Berlin's WWTPs are equipped with biological nutrient removal and effluent concentrations of 0.3 mg/L TP, 35 mg/L chemical oxygen demand (COD) and 0.4 mg/L NH_4-N can be achieved (Table 1), corresponding to an elimination of 97- 99% for these parameters.

Table 1: Mean concentration of typical parameters of raw sewage and effluent (advanced treated) of WWTP Schoenerlinde and irrigation ponds (2007-2010)

	TP [mg/L]	COD [mg/L]	TN [mg/L]	NH_4-N [mg/L]	NO_3-N [mg/L]	O_2 [mg/L]
Influent WWTP	14	900	83	63	-	-
Effluent WWTP	0.3	35	11	0.4	9	7.4
Irrigation ponds effluent (Ruehmland et al., 2008)	0.2	24.3	1.8	0.1	2-5	0.2

Estimates for the high nutrient and organic loads discharged during 80 years of irrigation field operation are shown in Table 2 and compared to current values.

Table 2: Volumetric flow Q and estimated nutrient (total phosphorous and total nitrogen, TP and TN) and chemical oxygen demand (COD) load in WWTP Schoenerlinde influent, effluent and irrigation water (*estimation: 25% of flow was discharged to irrigation field Buch)

	Q [m³/d]	TP load [kg/d]	COD load [kg/d]	TN load [kg/d]
WWTP influent	100.000	1.500	91.000	8.500
Historic irrigation field influent*	25.000	350	22.000	2.000
WWTP effluent	100.000	30	3.500	1.100
Current irrigation field influent	5.000	1,5	175	55

Due to the advanced treatment the load nowadays is reduced to only 2-4% compared to historic operation. Also, current total nitrogen discharge is mainly nitrate.

3.3 Results of surface water monitoring

3.3.1 Nutrients and organic compounds

From the beginning of the R&D project ELaN in 2011 to 2013, a regular monitoring was performed. The results will be discussed in the following sections. As shown in Figure 4, the surface water unaffected by the treated wastewater (OW1, compare Figure 1) contained median concentrations of 0.5 mg/L phosphorus, 2.1 mg/L ammonia, 1.5 mg/L nitrate and 22 mg/L total organic carbon (TOC), respectively. Median Concentrations in the WWTP effluent were generally much lower with values of 0.3 mg/L P, 0.2 mg/L NH_4-N, 8.2 mg/L NO_3-N and 12.7 mg/L TOC, respectively. At OW2, where an influence from the treated wastewater from the ponds was present, phosphorus and TOC concentrations were in the same magnitude. In the receiving river Panke (OWPu), the irrigation with treated wastewater resulted in an increase in TP from 0.15 (OWPo) to 0.32 mg/L (OWPu, 90-percentiles 2011-2013).

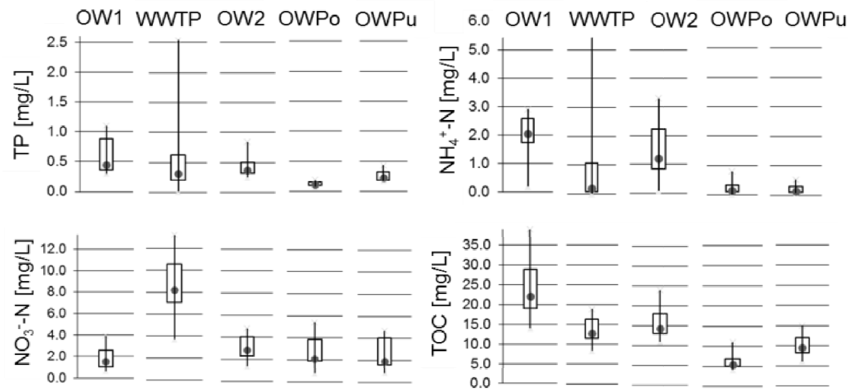


Figure 4: Nutrient (total phosphorous TP) and total organic carbon (TOC) concentrations along the flow path in surface water, including the wastewater treatment plant effluent (WWTP). The boxplots show median (point in box), 25- and 90-percentiles as boxlimits and min- and maxvalue as whiskers

For nitrate-N, the 90-percentile value in the Panke slightly increased from 3.9 (OWPo) to 4.1 mg/L (OWPu), for ammonium-N from 0.3 to 0.5 mg/L. Thus, the guideline values of the German directive for good quality in surface waters (LAWA) for TP (90-percentile <0.15 mg/L), nitrate-N (90-percentile <2.5 mg/L) and ammonium-N (90-percentile <0.3 mg/L) were not met. For nitrogen parameters, class II-III is met, for TP class III (elevated contamination).

In the polishing ponds, denitrification processes take place, resulting in decreased nitrate concentrations (Figure 5).

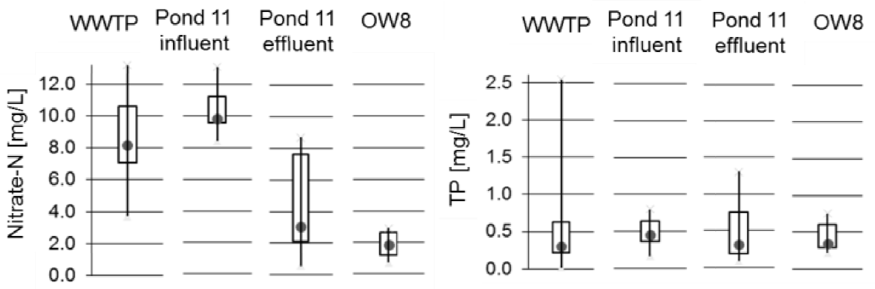


Figure 5: Nitrate-N and total phosphorous (TP) concentrations for wastewater treatment plant effluent (WWTP) and in- and effluent of pond 11 and outlet of irrigation site OW8. The boxplots show median (point in box), 25- and 90-percentiles as boxlimits and min- and maxvalue as whiskers

The nitrate-N concentration decreased from 9.9 to 3.1 mg/L (median values 2011-2013). For TP, no significant change in concentration was found.

3.3.2 Trace organic compounds (TrOC)

The behaviour of TrOC along the surface water flow path in the project area (Figure 1) is shown in Figure 6. Diclofenac is a widely prescribed nonsteroidal anti-inflammatory drug (NSAID), benzotriazole a corrosion inhibitor used in dishwashing agents and (AMDOPH) a metabolite of the NSAID dimethylaminophenazone.

OW1 in the north of the area was unaffected by treated wastewater irrigation. Concentrations of TrOC contained in high concentrations in treated wastewater (carbamazepine, diclofenac, benzotriazole) were below the limit of quantification. In contrast, AMDOPH had a median concentration of 0.13 µg/L. It was present in groundwater of the area in higher concentrations. In OW1, it was found because of an exfiltration of groundwater into the trench. In the receiving river Panke (OWPu), concentrations increased to 0.35, 0.08, 0.73 and 0.10 µg/L for carbamazepine, diclofenac, benzotriazole and AMDOPH, respectively. Before confluence of the trench from the irrigation area (OWPo), only benzotriazole was present with 0.05 µg/L (all concentrations are median values from 2011-2013).

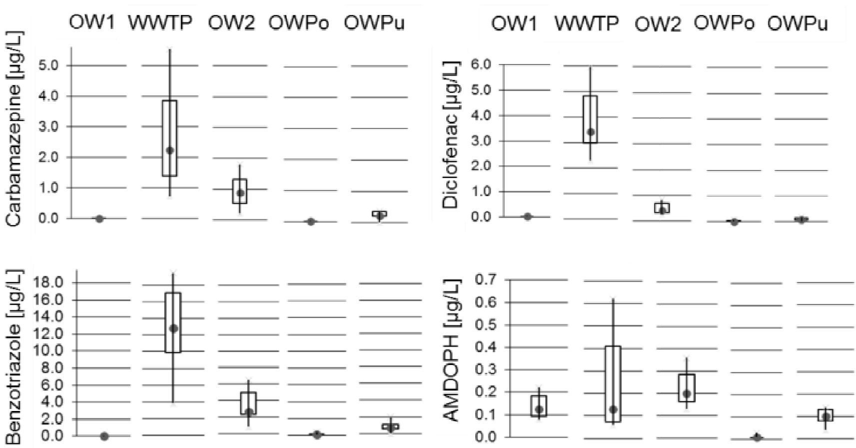


Figure 6: Concentrations of trace organic compounds along the flow path in surface water with wastewater treatment plant effluent (WWTP) and river Panke before and after irrigation influence (OWPo, OWPu). The boxplots show median (point in box), 25- and 90-percentiles as boxlimits and min- and maxvalue as whiskers

The anticonvulsant carbamazepine is known as wastewater tracer (Scheurer et al., 2011) because of its persistence. It was used to calculate the fraction of treated wastewater in river Panke (OWPu) as 10% (median value 2011-2013).

To study the potential of the polishing ponds for post treatment, in- and effluent concentrations of pond 11 were compared (Figure 7).

In the polishing ponds, median concentrations of carbamazepine and AMDOPH did not change significantly, due to their known persistence (Scheurer et al., 2011; Zuehlke et al., 2004). In contrast, diclofenac showed a strong decrease of 77%, which is mostly due to photodegradation (Buser et al., 1998). During the surface water passage from the pond effluent to OW8 (Figure 1), carbamazepine, diclofenac and benzotriazole decreased by 73-77% due to dilution. The AMDOPH concentration increased from pond effluent to outlet of the project area (OW8) by 87%, due to exfiltration of groundwater in the trenches.

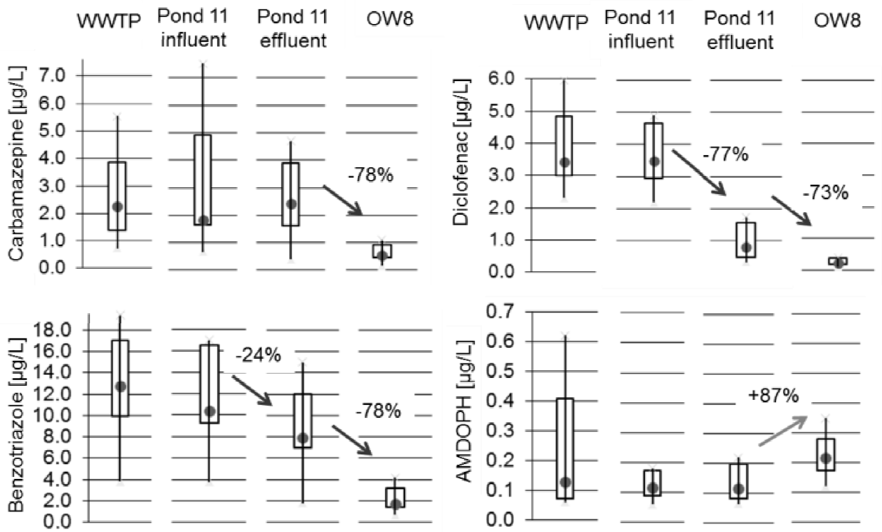


Figure 7: Concentrations of trace organic compounds for wastewater treatment plant effluent (WWTP) and in- and effluent of pond 11. The boxplots show median (point in box), 25- and 90-percentiles as boxlimits and min- and maxvalue as whiskers

3.3.3 Pathogens

In September 2013, the pathogens Escherichia Coli and Enterococcus, indicators for wastewater influence, were determined in surface water of the Lietzengraben (Figure 8).

At OW1, the spot unaffected by treated wastewater, a microbial contamination was already present (204 and 119 MPN/100 mL for enterococcus and E-Coli, respectively). This contamination could derive from birds or runoff water from agricultural land.

Comparing in- and effluent of pond 11, a degradation potential of the ponds for these pathogens was found. Concentrations decreased from 650 to 160 MPN/100 mL for enterococcus and from 5800 to 210 MPN/100 mL for E-Coli. The E-Coli increase from OW6 to OW8 and the Enterococcus increase from OW2 to OW6 were due to pastures for cattle situated next to the Lietzengraben. As OWPo and OWPu had pathogen concentrations in the same magnitude, the irrigation caused no additional contamination by pathogens for the river Panke. Comparing the pathogen reduction to literature values for ponds of 1 to 1.5 log values, it was lower. This was due the already low input concentrations.

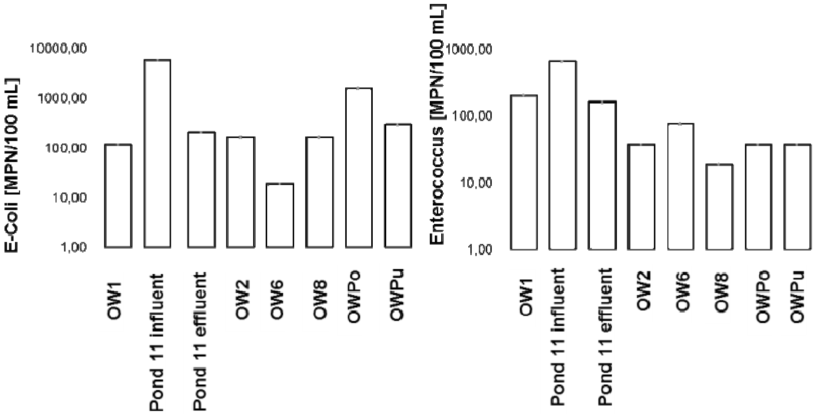


Figure 8: Escherichia Coli and Enterococcus in MPN (most probable number)/100 mL along the surface water flow path. The axis is in logarithmic scale

3.4 Outlook

Eco-toxicological tests were already performed and will be continued to contribute to the risk assessment of irrigation with treated wastewater. For a better understanding of processes in groundwater, a hydrological model will be developed.

Stakeholder involvement. A decision support manual for water reuse and its restrictions in Germany is currently written. Ensuring stakeholder participation, the R&D project aims to make a decisive contribution to the strengthening of society and the acceptance of water re-use. The developed decision support manual will include design, operation, and maintenance criteria for reuse systems under different perspectives. The use of this manual will help to establish flexible designs for managing wastewater in an environmentally sound manner. It is also intended to ensure that wastewater discharge is no threat to public health.

After the requirements for a sustainable wastewater treatment system have been discussed, the most appropriate technology option has to be identified for a particular region. For instance, the reuse of water for irrigation and production of energy crops can contribute to an increased share of renewable energy and combat climate change. While the water recovered from the subsurface will probably be of higher quality than the WWTP effluent, it might still be of lower quality than the local groundwater. Therefore, the system should be designed and managed to avoid intrusion into the native (local) groundwater and use only a portion of the aquifer. Technical solutions as well as constraints and limits for water reuse at the selected demonstration sites will be discussed. Also, the results will be linked with existing studies on wastewater reuse on a national (Braunschweig, Münster) as well as international level (e.g., the research project POSEIDON).

4. Conclusions

- Without discharge of advanced treated wastewater onto the irrigation fields, the ecosystem Lietzengraben would be regularly dry and biodiversity would be lost.
- Nutrient and organic carbon loads discharged today account to approximately 2-4% of the load applied for 80 years of raw sewage irrigation.
- The irrigation with treated wastewater had an impact on the receiving river Panke, nitrate, TP and some TrOC concentrations slightly increased. This was partly due to historic contamination from the former usage of the area.
- Compared to a direct discharge into surface waters, the polishing ponds and surface water passage in the project-area lead to a decrease of contaminant concentrations by degradation and dilution.
- The polishing ponds show potential in regard to post treatment for nitrate, some TrOCs and pathogens (E-Coli, Enterococcus).

References

Buser, H. R.; Poiger, T.; Muller, M. D. (1999). Occurrence and environmental behavior of the chiral pharmaceutical drug ibuprofen in surface waters and in wastewater. Environmental Science & Technology 33 (15), 2529-2535.

Ginzel, G., G. Nuetzmann & H. Handke (1995). Umweltgeologische Untersuchungen in einem ehemaligen Abwasserversickerungsgebiet (Rieselfeld) in Berlin-Buch. Mitteilungen der Österreichischen Geologischen Gesellschaft, 88, 61-67.

Gnirss, R., Sperlich A., Duennbier U., Moeller K., Taute T. (2011). Non-potable water reuse for landscape irrigation in Berlin, Germany. IWA WaterReuse conference Barcelona 2011.

Heberer, T., A. Mechlinski, B. Fanck, A. Knappe, G. Massmann, A. Pekdeger & B. Fritz (2004). Field Studies on the Fate and Transport of Pharmaceutical Residues in Bank Filtration. Ground Water Monitoring & Remediation, 24 (2), 70-77.

Huschek, G. (2005). Verbrauchsmengen von Humanarzneimitteln. In UBA (ed.), Arznei in der Umwelt - Zu Risiken und Nebenwirkungen fragen sie das Umweltbundesamt, Texte 29/05. . Berlin, Germany.

Looker, N. (1998) Municipal wastewater management in Latin America and the Caribbean : a discussion paper on trends, challenges and the market; prepared for the Round Table on Municipal Water, Vancouver, Canada, Mar. 15-17, 1998. IDRC Final Report. The International Development Research Centre.

LUA (2005) Umsetzung der Wasserrahmenrichtlinie - Bericht zur Bestandsaufnahme für das Land Brandenburg (Report on the implementation of the Water Framework Directive in Brandenburg). Landesumweltamt Brandenburg.

Marschner, B. & C. Hoffmann (2000) Mobilisation of heavy metals in soils on a former sewage treatment farm. First Intern. Conf. On Soils, of Urban, Industrial, Traffic and Mining Areas, Univ. Essen 12.-18.07.2000, pp. 275-380. Essen, Germany.

Massmann, G., A. Knappe, D. Richter & A. Pekdeger (2004). Investigating the Influence of Treated Sewage on Groundwater and Surface Water Using Wastewater Indicators in Berlin, Germany. Acta hydrochimica et hydrobiologica, 32(4-5), 336-350.

Möller, K., Burgschweiger J. (2008). Wasserversorgungskonzept für Berlin und für das von den Berliner Wasserbetrieben versorgte Umland (Entwicklung bis 2040), Berlin.

Rose, G. D. & C. International Development Research (1996). Community-based technologies for domestic wastewater treatment and reuse : options for uban agriculture. IDRC, Ottawa.

Ruehmland, S., M. Barjenbruch, H. Rustige & U. Duennbier (2008) Comparison of Six Constructed Wetlands and Ponds for Advanced Wastewater Treatment. International Conference on Wetland Systems Technology in Water Pollution Control. Indore, India.

Scheurer, M.; Storck, F. R.; Graf, C.; Brauch, H.-J.; Ruck, W.; Lev, O.; Lange, F. T. (2011). Correlation of six anthropogenic markers in wastewater, surface water, bank filtrate, and soil aquifer treatment. Journal of Environmental Monitoring 13, (4), 966-973.

Thierbach, A.; Limberg, J., Hydrostratigraphie in Berlin (2002). Korrelationen mit dem norddeutschen Gliederungsschema. Brandenburgische Geowissenschaftliche Beiträge 9, 65-68.

Wode, F.; Reilich, C.; van Baar, P.; Duennbier, U.; Jekel, M.; Reemtsma, T. (2012). Multiresidue analytical method for the simultaneous determination of 72 micropollutants in aqueous samples with ultra high performance liquid chromatography - high resolution mass spectrometry. Journal of Chromatography A 1270, 118-126.

Zuehlke, S. (2004). Verhalten von Phenazonderivaten, Carbamazepin und estrogenen Steroiden während verschiedener Verfahren (Behaviour of derivates of phenazon, carbamazepine and estrogen steroids during various methods of water treatment), Dissertation, TU Berlin.

Zuehlke, S., U. Duennbier & T. Heberer (2004). Determination of polar drug residues in sewage and surface water applying liquid chromatography-tandem mass spectrometry. Anal Chem, 76(22), 6548-6554.

Authors

F. Wode, R. Gnirss*, U. Duennbier*, K. Moeller **, F. Hecht***, T. Taute****

** Berliner Wasserbetriebe, Cicerostrasse 24, 10709 Berlin, Germany*

(E-mail: regina.gnirss@bwb.de)

*** Umweltvorhaben Dr. Klaus Möller GmbH, Berlin, Germany*

**** Freie Universität Berlin, Institute for Geological Sciences, Hydrogeology Group, Berlin, Germany*

Chapters from the topic of biological filtration and application

Béla Tolnai

Budapest, Hungary

“In practice, people are very reluctant to give up a theory in which they have invested a lot of time and effort"- Stephen Hawking

Content summary

The processes of water supply (water production and water distribution) and canalization (wastewater disposal and wastewater treatment) may be compared along system technical considerations. Regarding the canalization subprocesses there is no feedback, however, in the case of water supply it does exist. In providing the missing link, wastewater utilisation has to be spoken about in the future. Starting from this, the necessity of paradigm change may be deduced related to the activity in the wastewater branch. In order to maximize biogas yield, modifications in the widest possible sense are needed thus replacement of activated sludge technology also emerges. The possibility of taking this step was provided in relation to modeling bank filtering.

By the help of the new approach the insufficiencies of presently predominant procedures may be highlighted, and the issue of the possible dimensioning of biological spaces based not only on experience may be outlined. By means of system technical considerations a more efficient water treatment technology may be reached.

Keywords:

bank filtration, water treatment, biological filtration, modeling, dimensional analysis

1. The biological life

"Organisms are different from non-living things in many respects. One of their most striking characteristics is their ability for reproduction, which brainstorms both human fantasy and scientific approach even today ...," - writes Thomas Junker in his book “The history of biology”. The ability of microbes to reproduce is one of their preconditions to survive too. In aqueous environment, having favorable conditions their life will certainly develop. With other words, if the conditions of nutrient supply (logistics) and the conditions of the environment (climatic) are available then microbial colonization will take place on the solid surfaces in contact with the water. The solid surface may be a sand layer of a river, a high surface area filter medium, the roots of plants, a membrane bundle placed into the water, the trickling filter, or any surfaces of suspended materials floating in the water (river water or waste water).

Concerning biological life, in industrial water practice there are two main lines of activities. There are cases when we are trying to prevent biological life. Disinfection means inhibition of life. However, there are goals when we try to stimulate biological life. The bacteria implemented nutrient degradation belongs to this category.

Modelling of the biological filtration process is possible, and the same model may be used both for the inhibition and for the promotion of the bacterial life, as shown below.

2. The model of biodegradation

Biodegradation is a complex process dependent on many variables. In such processes, it is worth to choose dimensional analysis for the modeling. In the following the general method described by Thomas Szirtes [7] is used.

This dimensional analysis is made in two-steps. First the independent variables of the process are listed and sorted into dimensionless groups, and in this way the number of the dimensionless variables is smaller than that of the original ones. The variables may be found in the matrix of dimensions:

		ΔS	v	w	D_{O2}	E_h	L	F	T	R	D_S	C_{O2}	d	
	m	-3	2	1	2	2	1	0	0	2	2	-3	1	
B	kg	1	0	0	0	1	0	0	0	1	0	1	0	**A**
	s	0	-1	-1	-1	-3	0	1	0	-2	-1	0	0	
	K	0	0	0	0	0	0	0	1	-1	0	0	0	
	A	0	0	0	0	-1	0	1	0	0	0	0	0	
	mol	0	0	0	0	0	0	-1	0	-1	0	0	0	
	Π_1	1	0	0	0	0	0	0	0	0	0	-1	0	
	Π_2	0	1	0	0	0	0	0	0	0	-1	0	0	
D	Π_3	0	0	1	0	0	0	0	0	0	-1	0	1	$C = -(A^{-1}B)^T$
	Π_4	0	0	0	1	0	0	0	0	0	-1	0	0	
	Π_5	0	0	0	0	1	0	1	-1	-1	0	0	0	
	Π_6	0	0	0	0	0	1	0	0	0	0	0	-1	

Figure 2-1: The matrix of dimensions and the matrix of the results

The relevant dimensional variables in the above matrix are as follows:

Table 2-2: The dimensional variables

Variable name	Sign	SI dimension
Nutrient degradation rate	ΔS	kg/m^3
Kinematic viscosity	ν	m^2/s
Filter speed	w	m/s
Diffusion coefficient of oxygen	D_{O2}	m^2/s
Redoxpotential	E_h	$m^2kg/s^3/A$
Biologically active layer thickness	L	m
Faraday constant	F	As/mol
Abszolute temperature	T	K
Molar gas constant	R	$m^2kg/s^2/K/mol$
Diffusion coefficient of substrate	D_S	m^2/s
Dissolved oxygen level	C_{O2}	kg/m^3
Size of standard particle	d_m	m

In Figure 2-1. the results matrix is also included, which is determined by matrix algebra. The obtained dimensionless numbers are as follows:

Table 2-3: The dimensionless numbers

Dimensionless number	Name
$\Pi_1 = \Delta S / C_{O2}$	Ratio of concentrations
$\Pi_2 = \nu / D_S$	Sc-number (Schmidt)
$\boldsymbol{\Pi_3 = w\, d_m / D_S}$	**Pe-number (Peclet)**
$\Pi_4 = D_{O2} / D_S$	Ratio of diffusion coefficients
$\Pi_5 = E_h F / RT$	Ne-coefficient (Nernst)
$\boldsymbol{\Pi_6 = L / d_m}$	**Geometric ratio**

These dimensionless numbers can be further categorized. The Pe-number and the L/d geometry ratio are those which we are able to influence by certain operations, while Π_2, Π_3 numbers has indirect, and the Π_5 coefficient has direct temperature dependence.

In the second step of the dimensional analysis, using the dimensionless numbers the relationship describing the phenomenon can be created. Along heuristic considerations the following function can be introduced:

$$\Delta S = \mu(Pe)\, C_{O_2}\, \frac{1}{Pe}\, Sc\;\; rH\, \frac{L}{d_m} \qquad (2.1)$$

where

rH dimensionless ORP derived with the help of Π_5 (Nernst-coefficient) and pH

μ(Pe) biological filtering coefficient.

3. The conditions of biodegradation

3.1 Logistics conditions

The biofilm is the living space for microbial communities, for which a solid surface is required to attach with. The solid surface is called the biofilm holder. The biofilm holder may stand or move. In bank filtration the sand grains are standing, and the biofilm is formed near the riverbed, where the water velocity is the slowest.

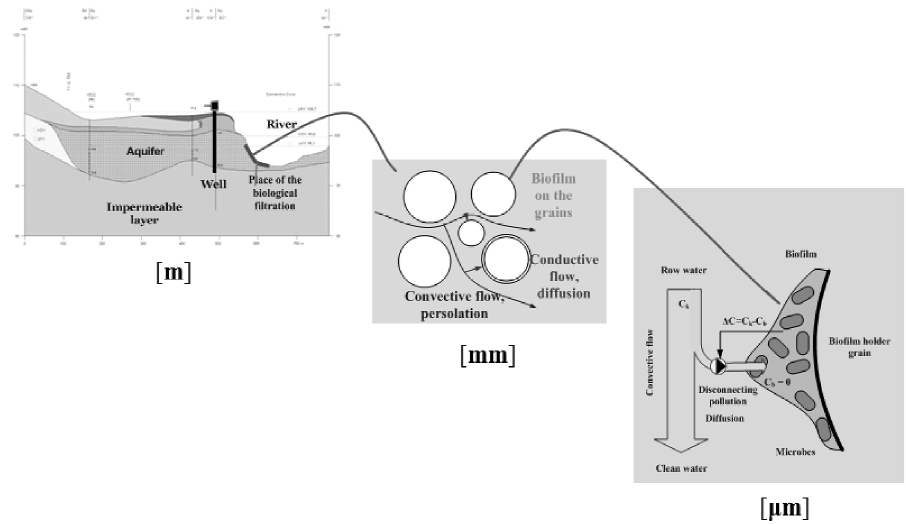


Figure 3-1: The bank filtration process

After attachment the microbes do not change their positions. Keeping them alive should be taken care by nutrient supply. The logistics task consists of two stages. The convective flow transports nutrients to the biofilm, and the conductive flow delivers them into the biofilm. The convective flow is driven by pressure difference, which at bank filtration is maintained by continuous pumping. The conductive flow or diffusion is driven by concentration differences. The concentration difference is understood between the waterbody and the biofilm. The concentration difference will be then constant when the degradation established within the biofilm, i.e. the biochemical reaction proceeds.

Thus the nutritional degradation logistics is made by several steps in series, and feedback can also be found in it (Table 3-2).

Biochemical reactions at the end of the line can only be achieved if the preceding phases have already been met. The biochemical reactions (nitrification and other degradations) are taking place within the biofilm.

Table 3-2: Serial proceeding and feedback

Serial proceeding

Partial process	Driving force	Maintened by
Convective flow (to the biofilm)	Pressure difference	Pumping
Conductive flow, diffusion (into the biofilm)	Concentration difference	Work of bacteria
Bio-chemical degradation (inside the biofilm)	Redox envinronment	Live-drive of bacteria

Feed-back

Considering only the diffusion phenomena, first the smallest molecular components should fall into the biofilm. However, this is not always the case. Maintaining of the concentration 3difference depends on the activity of the bacteria. There are some bacteria, which need coal for "work". However, the carbon from degradation high-molecular substances is also extracted from the water. Consequently the breakdown of large molecules thus may precede that of the smaller ones, thereby creating a kind of feedback.

The block diagram of the nutrient degradation process is as follows:

dissolved O_2 + organic substance → $\boxed{\text{microorganisms}}$ → CO_2 + biological growth

Figure 3-3: Mechanism of biodegradation

Based on this mechanism oxygen and organic nutrients must be injected into the biofilms formed by the microorganisms. This is the precondition of the logistical process of nutrient degradation.

The oxygen diffusion coefficient is about $20*10^{-10}$ m^2/s in size. This is a high value, significantly greater than that of the substrate. The oxygen diffuses easily, for the substrate it is difficult.

The water may be originated from different sources, though a characteristic molecule (or atomic formations) can be found in it [10]:

$$\mathbf{(CH_2O)_{106}\,(NH_3)_{16}\,(H_3PO_4) + 138\,O_2 =}$$

typical mulecule *oxygen*

$$\mathbf{106CO_2 + 122H_2O + 16NO_3^- + HPO_4^{2-} + 18H^+}$$

carbon dioxide *water* *harmless substances*

Figure 3-4: Characteristic atomic formations

Succinctly the following statements may be formed about this stochiometric formula:

- The degradation requires a lot of (!) oxygen.
- The end product is mostly water and carbon dioxide as well as slightly other "roughage".

The nutrient degradation is therefore a "filter", which makes the materials located in the water not only separated - i.e. filtered - but they are transformed into materials (water, carbon dioxide) which can leave the biofilm easily, without causing further contamination of the water.

With the size of molecule one can estimate the diffusion coefficient of the substrate, having an order of magnitude ranges between (2-7) * 10^{-10} m^2/s. The proportion of diffusion coefficient of oxygen to that of the substrate is on average about four.

For "industrial scale" nutritional degradation, in addition of a continuous nutrient supply, to settle sufficient number of microbes a surface of sufficient size is also required. In a given volume the smaller the d_m, standard diameter of the biofilm-holder the larger is its available surface area. (Since identical smaller objects have larger total area.)

The nutrient supply logistics and the size of surface area is characterized by the Pe number.

$$\mathbf{Pe} = \frac{\overset{operating\ \ characteristics}{}\quad \mathbf{w}\ \mathbf{d}_m \quad \overset{filter\ layer\ (biofilm-holder)\ propertie}{}}{\mathbf{D_S} \quad _{propertie\ of\ \ the\ water}} \tag{3.1}$$

where

w	velocity of filtration
dm	standard grain diameter
Ds	diffusion coefficient of substrate

The Peclet number, as the ratio between convective and conductive material flows, provides also some information about the size of the bacteria-populated area.

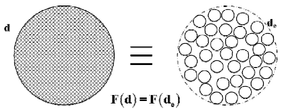
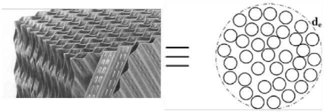
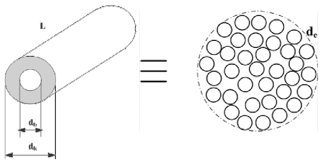
A dimensionless number can be considered as a similarity criterion, only if it is a coefficient of the non-dimensional differential equation describing the biodegradation. Theoretically, by solving the Navier-Stokes and the transport differential equation system the velocity-pressure-concentration relations can be determined in the space and time. Solving the differential equations meets obstacles since the complexity of the initial and boundary conditions, and also the continuous reproduction of the material degradation to be included in the boundary conditions are not clearly understood as yet. In the dimensionless form of these assumed differential equations the Pe-number is a coefficient. Therefore, the Pe-number is a similarity criterion of the biological filtration.

Despite the biofilm-holder structures differ radically, within the biofilm layer the biodegradation caused by the microbes is assumed here to be the same. Depending on the logistics conditions, the measure of the degradation, that is the efficiency of the biological filtration may be different, but the similarity of the procedure, in case of various water treatments is maintained through the same size of the Pe-number.

About bank filtration it is known that drinking water quality is produced from the not exactly clean Danube water in one step as learned from the more than 100 years experience in Hungary. The favourable conditions of bank filtration are obtained with Pe-numbers between 10 and 20. The bank filtration mechanism is mainly biodegradation. Therefore, other biodegradation technologies are discussed below as compared to the bank filtration, which proved to be very effective.

The calculation of the Pe number is simple only for bank filtration. For other known biodegradation processes considerations must be made mainly as regards the equivalent grain size geometry. The following table shows the determination of the equivalent and the standard particle size.

Table 3-5: Determination of the equivalent particle

Type of biofilm holder	Parameters	Size of equialent particle
	Specific surface: a [m^2/g] Size of granules: d [mm] Density: ρ [kg/m^3]	$d_e = 6\frac{V}{F}$
	Block surface: a [m^2/m^3] Block density: ρ_t [kg/m^3] Material density: ρ [kg/m^3]	
	Fiber geometry $V = \frac{(d_k - d_b)^2 \pi}{4} L$ $F = d_k \pi L$	

As can be seen in this table the biofilm adhesion has been achieved with widely different geometrical forms. For the sake of the comparison of the different cases to the sand particles of the bank filtration, only spherical form sand particles are assumed, and basically only the outer surface of the sand layer is considered. The comparison is based on the fact that the biofilmhoders 'volume per surface ratio' is equivalent to what size of sand grains have. If the equivalent diameter is larger than the size of microbes, then the standard particle diameter d_m will be the same as the equivalent grain diameter, $d_m = d_e$. While, if the size of microbes is larger, than the standard particle size is selected to be five times the average size of the microbe. The suitability of this arbitrary ratio is based on the Figure 3-6.

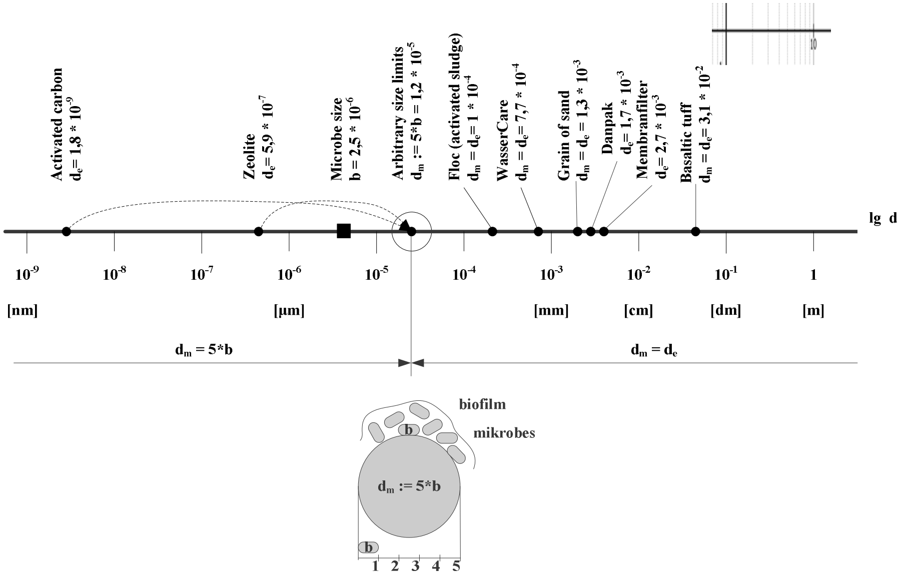


Figure 3-6: Explanation of the arbitrary choice of the standard diameter dm

Figure 3-6. shows the equivalent and standard particle size of the different biofilmhoders in logarithmic scale. If the equivalent diameter is smaller than the size of bacteria, then the bacteria can inhabit only partially the available surface. Therefore, the artificial plastic filters must be fitted with larger surface areas. Equivalent diameter smaller than the average size of bacteria is unnecessary to achieve because the surface will not be exploited.

The filtration velocity, w in Equation (3.1), is identified with the quotient of the volume and the filter cross-sectional area. Even in the well known case of bank filtration the speed-increasing effect due to the void coefficient is not considered in the calculation.

At bank filtration the convective velocity is defined as the velocity of the moving water to the standing biofilm. This velocity can be calculated easily. At the activated sludge technology both the water and the sludge are moving. In this case to estimate the magnitude of the relative velocity is also difficult.

The filter velocity of bank filtration is very low, w = 0,1 – 0,3 m/d. This is not a sensible value. However, at the activated sludge technology the velocity due to mixing and the air supply is significant. It can be estimated visibly.

The activated sludge technology has oxic and anoxic basins. One of them obtains air "blows", while the other does not, and this role is periodically alternated. If air intake is done, the basin is oxic, if not it is anoxic. But is this really the difference? The air intake cause increased convective velocity in the oxic basin. As a result the diffusion conditions are worsening.

In the anoxic basin the "disturbing" velocity component is missing, there is time for diffusion and the degradation will be continuous until the dissolved oxygen is there. Besides these, processes that do not require oxygen also occur.

In the theory of the residence time (sludge age, contact time) used in dimensioning of equipment only the fact of the movement is important, not its velocity. By way of illustration let us take up two cases that have the same residence time.

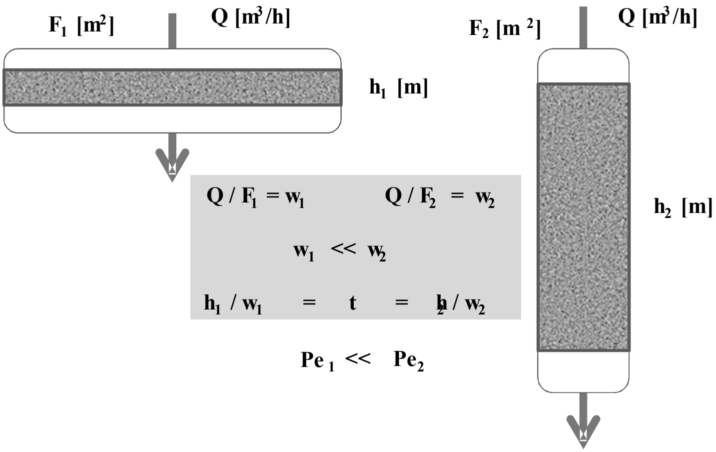


Figure 3-7: Comparison of filters with the same residence or contact times

Despite the same residence time the two cases are not the same because the Pe number is highly different.

Diffusion plays an important role at adsorption and at biological filtration as well. The diffusion takes place rather in the case of the larger cross-sections, and at higher filtration speed probably there is not enough time to the formation of the diffusion.

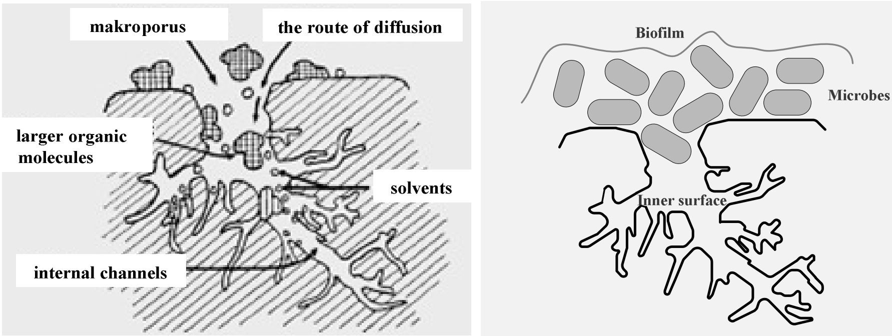


Figure 3-8: Adsorption and biodegradation

It is the concentration difference that drives the contaminants or the nutrients into the crevices of the solid material. With time the concentration differences between the outer and inner spaces are more and more equalized by the adsorption. When reaching the equilibrium condition, the filter layer (active carbon) is required reactivation. If the same filter medium plays a biofilmholder role, then the concentration difference due to the biological activity is continuously replenished by the degradation of the nutrients.

On right hand side of Figure 3-8. it can be clearly seen that inner surface by biofilmholder "application" is not fully utilized because of the size of the bacteria inhibits to inhabit the inner spaces. The recognition of this fact has led to make the distinction of the equivalent and standard particle size.

At bank filtration cleaning of the filter layer happens on a natural way. The small amount of roughage is rinsed twice a year after floodtime.

The biological filtration technologies are compared in the table below. Real and hypothetical cases are also included in the table.

The biological filtration has not yet been a comprehensive theory. For procedures based on the biodegradation mechanism the Pe-number has not been calculated. Table 3-9 is an attempt based on available data to do this. It may immediately been stated that the advantages and disadvantages of the individual methods may be explained by the numerical values of the similarity criteria. However, naturally many measurements and tests are sought to establish more accurate filtering theory.

Table 3-9: Different biofiltrations

Nr	Biological filtration	D_S [m^2/s]	d_e [m]	d_m [m]	w [m/s]	w [m/h]	Pe [-]	Comment
1	Bank filtration	1,5e-10		1,5e-3	1,2e-6		10	Produces drinking water quality
2	Bank filtration at low water level	1,5e-10		1,5e-3	2,4e-6		20	Is moderately effective
3	Ammonia removal on rapid filter	19,4e-10		1,5e-3	8,8e-4	3,16	670	Filtermedia is sand can not operate effectively under rapid filtration conditions?!
4	Activated carbon filtration	5,0e-10	1,8e-9	1,2e-5	3,5e-3	12,6	34	Sometimes worms, protozoa appear
5	Aktivated sludge wwt	1,5e-10	0,1e-3	0,1e-3	???		???	Inefficient?! 18x larger reactor dimension
6	Trickling filter wwt 240 m^2/m^3	1,5e-10	7,7e-4	7,7e-4	2,8e-4	1	1440	In spite of the optimal air intake is not effective?
7	Tricklingfilter wwt with ozon dosage	5,0e-10	7,7e-4	7,7e-4	2,8e-4	1	432	More effective ?!
8	Wwt on zeolite bed filter	5,0e-10	5,9e-7	1,2e-5	4,2e-4	1,5	10	10-15 microns of biofilmholder porosity would be sufficient !
9	Membran filtration	1,5e-10	2,7e-3	2,7e-3	1,0e-5		187	Not develop meaningful biology

3.2 Environmental conditions, climatic characteristics

Inside the biofilm the completion of desired biochemical reactions depends on the microbes. The degradation efficiency is also a consequence of microbial activity. Under climatic characteristics properties related directly to the activities of the bacteria is ment. Those environmental factors are listed here that determine the settling of the voracious microbes as well as their appetite after their attachment.

Louis-Claude Vincent the French anthropologist and water researcher established the Vincent diagram based on the pH and rH levels to identify the diseases caused by bacteria. According to him, the fight against these diseases means shifting the climatic conditions in a position where the microbes can no longer feel good themselves, whereby the bacteria and with them the disease dies out. This item should be hold vice versa. If you want to get the bacteria eagerly participate in the degradation of nutrients, such conditions must be created, what they like, where they feel comfortable.

The pH is a dimensionless number, the rH is interpreted as dimensionless redox potential, which has the formula:

$$\mathbf{rH} = \frac{\mathbf{2\,E_h}}{\vartheta\,\mathbf{T}} + \mathbf{2\,pH} \tag{3.2}$$

where $\vartheta = 2{,}303 \cdot \dfrac{R}{F}$ = 0,1984 mV K^{-1}

The range rH is 0 – 42, values between 0 – 15 indicate strongly reducing system, the interval 25 – 42 indicates strongly oxidizing feature. The larger the value rH is, the medium has stronger oxidizing effect.

Based on this relationship it is clear that rH depends on the redox potential Eh, on the absolute temperature T, and on pH. The everyday use of the rH value in the water treatment is not a well-established practice; sometimes even its scientific acceptance is debated. Nevertheless, the Nobel-prize winner Francois Jacob French doctor has classified the different micro-organisms according to the rH.

rH = 0 – 7,4	reducing (fermenting) anaerobes
rH = 7,4 – 14	microaerophilic microorganisms
rH = 14 – 42	oxidation (breathable) aerobic microorganisms

As the pH = 0 – 14 range is very wide, so the rH = 0 – 42 scale has also a very large "distances". In the fields of the drinking water and the waste water treatment both variables can only move in a narrow range.

For users with practical aims there is no reason to doubt the importance and usefulness of the rH measure. Therefore in Figure 3-10 this concept is freely used.

Following the example of the Vincent diagram, in the coordinate plane spanned by the rH and Pe variables, the typical microbial compositions may be attached to the A, B ranges.

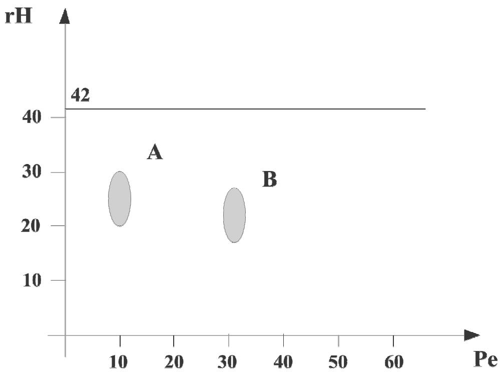


Figure 3-10: Ranges on Pe - rH

4. System technical consoderations

4.1 About the history of wastewater disposal

The branch of canalization consists of wastewater disposal and wastewater treatment. The establishment of the systems spans decades and centuries. In densely populated settlements, the establishment of canal networks was started due to the drainage of internal water and prevention of epidemics. The end point of rainwater drainage and wastewater disposal is the receiving river (Figure 4-1/A). The only aim of the constructed canals was to drain water.

The construction of multi-storey blocks of flats resulted in the general spreading of flush toilets. For the disposal of communal wastewater no separate network was established, drain connections were made to the existing canals (Figure 4-1/B). The end point of the so established unified canal network still remained the river, despite the fact that water pollution significantly increased.

A considerable decrease in the self-purification capacity of rivers raised the necessity of purifying wastewaters, as a result of which wastewater treatment plants were established (Figure 4-1/C).

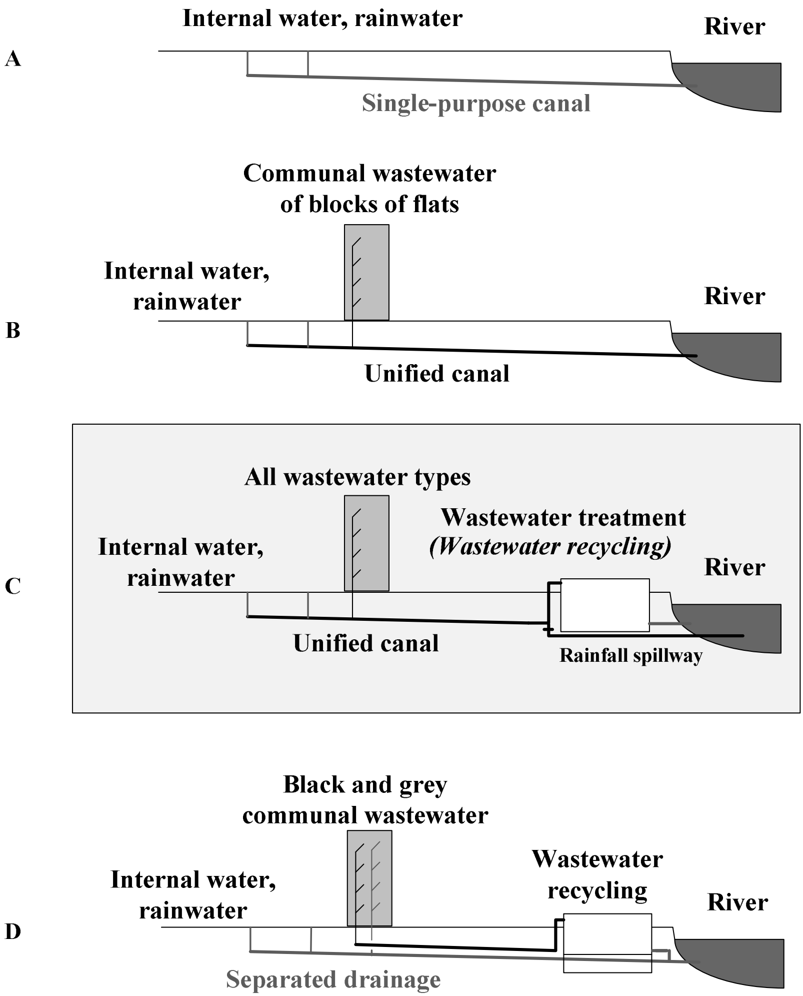


Figure 4-1: The development of wastewater disposal and wastewater treatment

The capacities of wastewater treatment plants are determined based on the volume of wastewater arriving at the plant. In order to decrease dimensions, the idea of establishing a separated canal system was raised. Separate collection of rainwater and communal wastewater means different end points. Rainwater would have got directly into the river without purification, whereas communal wastewater would have gone to the plant. The high costs of establishing a dual-network strongly hindered and hinders today as well the spreading of separated canals. However, for rational reasons wastewater plants are not dimensioned for peak loading. Drainage of rainfall loading happens through a spillway. At this time a part of wastewater diluted by rainwater gets into the river without purification. This solution could not be objectionable from the aspect of environment protection as rainfall peaks occur in an insignificant percentage of the yearly number of hours. The loading of living (river) water is far within its self-purification capacity.

The fee of the water public utility service was cheep in the past (far below its prime costs, at least in Hungary, before the change of the economic system). This fact led to wasting water but a more serious consequence was that capacities were determined according to this condition as well. Following the change of the economic system (in Hungary) the price of water became a market price, which led to the decrease of public water consumption thus to reduced water volume appearing in the canals. The appearance of tax contents realized in the price, directly not serving water public utility service, resulted in an even more significant extent of decrease, which reached 40-60%. Due to this, the dwell time increased on the canal system side, which resulted in an intensive odour effect of the canals. The canal system works as a biological reactor. Low water volume also promotes dry substance sedimentation. In the case of a rainfall, the increased water volume washes out the canal system thus the water let out through the spillway does not belong to the category of diluted wastewater, but to the category of wash-water with highly concentrated pollution. Contrary to the dimensioning effort determining the capacity of the wastewater plant, the realized environmental loading may not be considered moderate. The incorrectly interpreted water price policy relies on the self-purification capacity of nature.

Water supply again and again raises the dilemma of putting drinking water or pure water into the network. In the Western value system only network water of drinking water quality may be accepted despite the fact that the internal use of water only accounts for an insignificant proportion of total water use. The Asian approach is more permissive or more economical and demands only ‘pure’ water quality for network water. It says internal use of people always has to happen after boiling. Similar dilemma is faced in the case of wastewater as well. Separation of wastewaters by quality runs into considerable infrastructural thus financial difficulties. The separation of rainwater and wastewater was brought up by the requirement for a reasonable dimensioning of the wastewater plant. Contrary to the effort for separation, the emphasis is on the purification of wastewater.

According to another concept, separation is reasonable in respect of the so called grey and black waste waters, which starts from the demand for waste water recycling. The blackwater (urin+faeces) contains the 99% of bacteria, the 98% of nitrogen and the 90 % of phosphorus.

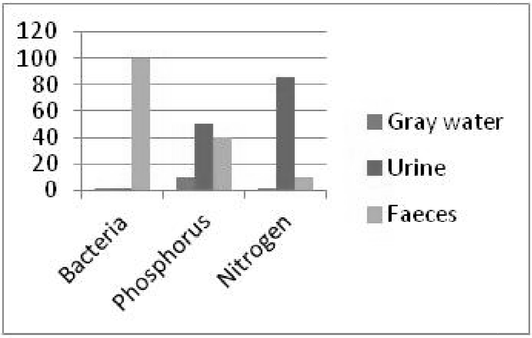


Figure 4-2: Parameters of grey and black (urine+feaces) wastewater (Source: Tolilettes Du Monde, 2009)

The category of grey wastewater means that it does not contain the faeces portion that is produced by the use of flush toilets. The latter is also called black wastewater. Grey wastewater only contains 1/9 of the pollution of black wastewater thus its purification only needs some treatment. However, the grey to black wastewater volume ratio has a reverse trend, black wastewater represents slightly more than 10%. Faeces-free grey wastewater is defined by the no. 12056-1 European Standard as slightly dirty wastewater.

Starting from the separation of either rainwater – communal wastewater, or grey – black wastewater, the establishment of a dual-network would be needed. The extremely high costs of establishment, as well as the already established century old canal systems classify subsequent separation into the category of utopia (Figure 4-1/D). In reality the wastewater collected in the unified network has to be counted with. As for regulation, the only issue to be raised is that industrial wastewaters should not appear in the canal network as their efficient purification can be solved and should be solved rather locally as the materials getting into the water during the technology are precisely known. In this case only the combination of communal wastewater produced as a mixture of grey and black water and rainwater appears in the canal network.

However, the wastewater arriving at the plant in the new approach is not considered as wastewater but as raw material from which valuable materials may be recovered. This also raises the issue that the principle of “the party causing pollution has to pay” is not sustainable due to the simple reason that the communal consumer using canal network service is not the party causing pollution but a basic material supplier. Water as medium plays a logistic role which is used up during the execution of the task. It dissolves a certain quantity of the carried material. Following the separation of the recoverable materials, disposal of the remaining pollution is a pre-requisite of admission into living water.

The spirit of this new approach also needs changing water public utility terminology.

4.2 Terminological interpretations

It is widely known that by following the course of water, both branches consist of two clearly separable processes. In the case of water supply, the water production is followed by water distribution, and the subprocesses of canalization: wastewater disposal and wastewater treatment. In addition to this, water supply has a very live feedback, according to which the quality of supplied water has to be guaranteed on the water distribution side, but this may only be influenced in merit on the water production side. Feedback is implemented through water quality.

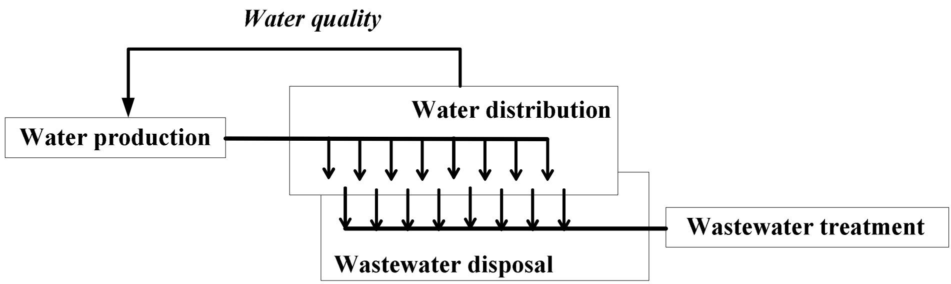


Figure 4-3: The missing feedback

Canalization is not such a process. Wastewater disposal collects the produced wastewaters and allows them to arrive at the wastewater plant. Then the wastewater treatment process tries to purify water according to the prescribed limit values. Between these two subprocesses there is no feedback in the sense as it is in the case of water supply.

If the missing feedback is provided, the orientation of the task in the plant is changed. The supplementation is only possible if the concept of wastewater treatment is replaced by wastewater recycling.

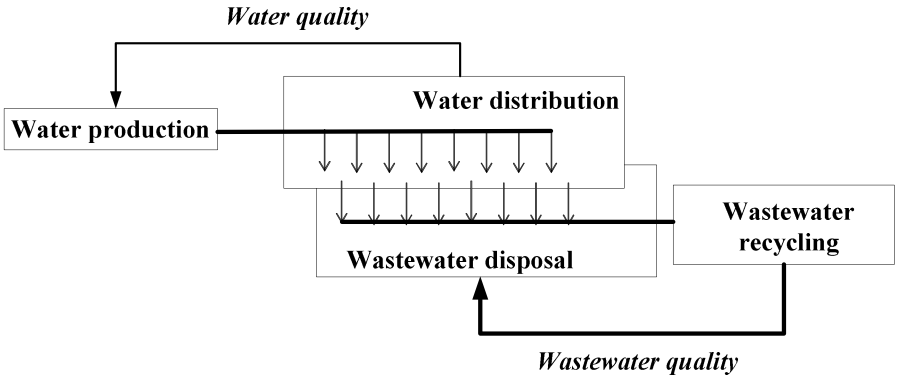


Figure 4-4: Providing the missing feedback

If this paradigm change is implemented, the quality of the wastewater arriving at the plant does make a difference. Wastewater disposal receives an objective function. It is important that it should not be the canal system that works as a biological reactor, and the energy content of wastewater should not be wasted there but the organic material and the medium carrying it should reach the plant as soon as possible.

At this point wastewater energy content should be focussed instead of wastewater loading. The aim is utilisation and recovering the most possible energy. This change of approach needs giving up the previous practice.

4.3 Where is the point of intervention?

The paradigm change does not keep the scope of wastewater treatment, or wastewater utilisation as referred to in the new technology within the wastewater plant, but manages it at system level. Accordingly, it also searches the group of possible interventions in the field of wastewater disposal.

It does not mean relocation of the main points in the activity chain but radical alterations of activities in the given field.

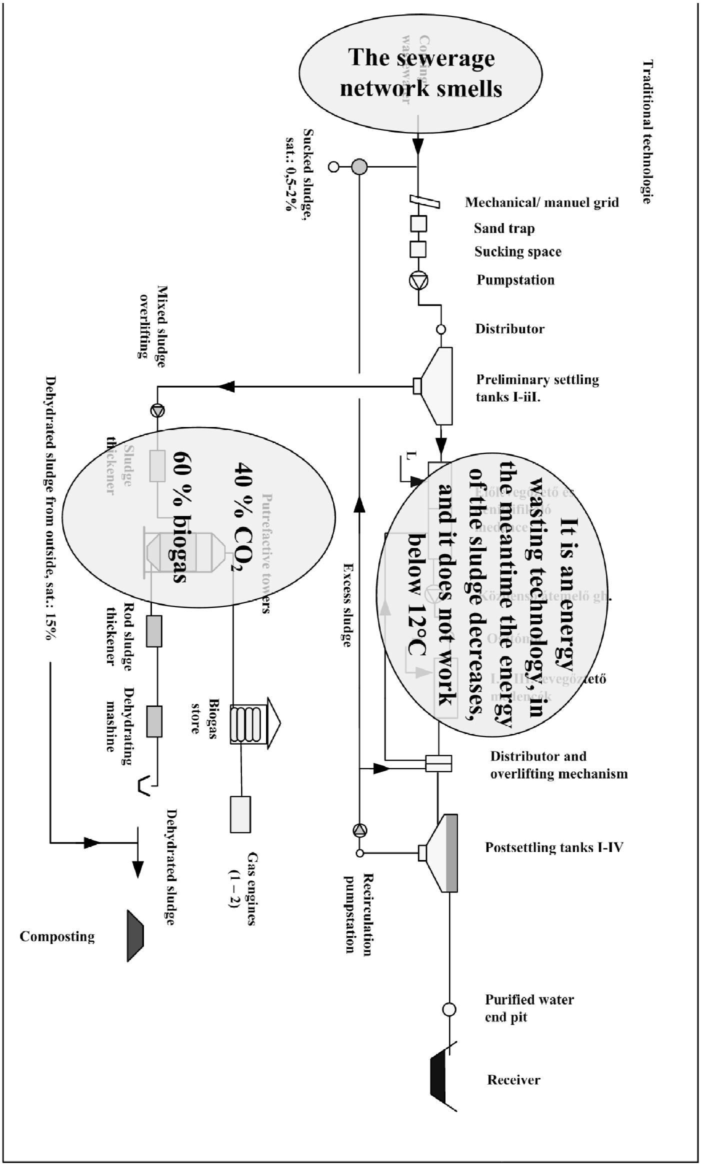


Figure 4-5: Intervention possibilities

Figure 4-5 shows a traditional (activated sludge) technological line, in which the places are indicated where changes in merit in the sense of the above written are needed.

4.3.1 Objective function of wastewater disposal

Regarding the so far wait-and-see canal network operation policy, in the future wastewater should be expected to lose as little energy content as possible along its course, i.e. dwell time in the network should be as short as possible. The objective function described in this form exposes a task on both the designer and the operator. When establishing new canals, the designer has to reconsider slopes, the method of arrangements, whereas the operator has tasks in relation to harmonising the operation of pumping stations.

However, the price authority also has a lot to do. When determining the fees, the operation of wastewater disposal “based on water logistics” has to be taken into consideration, or more precisely its operability. The water closet works with water. And in a system thus established the presence of sufficient water volume is a prerequisite. If it is missing, dwell time increases, the odour effect of canals will be strong, due to which recoverable energy may only be less. The volume of water appearing in the canal system may be most influenced through fees. In the last period the increase of fees – also through charging with taxes – led to a significant decrease in water consumption. The rate of decrease exceeds 50%. The not properly considered method of increasing water and drainage fees thus might lead to a negative technological effect.

4.3.2 The utilisation of sludge

Producing biogas and composting the remaining proportion

By means of rotting, biogas may be obtained from sludge. The maximization of biogas yield requires that the whole amount of sludge should undergo rotting after pre-sedimentation. This also means that a water purification technology is required that does not use sludge in its operation.

After a proper preparation the sludge gets into the so called rotting towers. Rotting happens among anaerob conditions, and during this biogas (a mixture of methane and carbon dioxide) is produced, and wet sludge deprived of its energy is left in its solid state. Due to its high (approximately 40%) carbon dioxide content, biogas has to be purified by means of a rather expensive method.

The question has to be raised: is it cheaper to prevent carbon dioxide from getting into than to extract it? The essence of sludge preparation is dehydration. The shaking tables and presses execute sludge thickening by a physical principle. However, neither shaking nor pressing happens by excluding air. Consequently, the thickened sludge during these operations absorbs a considerable amount of oxygen, which then deteriorates anaerob conditions in the rotting tower thus promoting the increase in the carbon dioxide content of biogas.

Probably the carbon dioxide content of biogas cannot be totally eliminated, however, the content may be decreased, and the prevention of its getting into or appearing surely needs lower investments than subsequent removal.

Rotting towers have to be heated, which is a condition for operation, and in addition to this sludge content has to be mixed continuously. Waste heat of gas engines can also be used for heating. However, the heat quantity, sometimes unnecessarily produced, may be utilized for drying the sludge to be composted. The often used solar drying seems to be cheap, however, it is less intensive.

Composting the whole amount of sludge

There are some opinions according to which biogas production is not the right method of utilising sludge. These state that the whole sludge amount has to be composted. Using the compost in agriculture is a fundamental interest of mankind as thus soil erosion can be prevented and the food producing capacity of the Earth can be preserved.

This idea raised the necessity of separating grey (soaped) and black (faecal) wastewater and gives sense to this. Grey wastewater practically has to be treated only, the purification of black wastewater is not grounded in this approach as now the aim is to maximize the compost amount.

In big cities the subsequent separation of grey and black wastewaters could only be implemented with great investments. As a remaining option, this may be corrected in the wastewater plant to the extent that from the preliminary clarifier the whole sludge amount is directed to the sludge line. Thus the whole sludge amount is totally composted. The remaining water used up during the logistic process (used water) is purified. This water only contains solute pollution.

Burning of the sludge

Some are against composting of the sludge. In the case of city wastewaters collected through unified system canals, the quality of admitted wastewaters is not sufficiently checked. The incoming water may contain heavy metals, spent oil, etc. Therefore composting then disposing in arable lands is excluded as agricultural lands would become contaminated this way. Therefore they say burning the sludge to be a better alternative as it also happens to grid waste as well.

Naturally, this opinion is based on reality, and at this point the opinion saying “it is not the quality of wastewater that is important but that it should be paid for” becomes unacceptable. The tasks of authority may be designated here for the protection of nature. The water quality of admissions has to be checked by the Environmental Protection Authority the same way as it is done by the National Public Health and Medical Officer Service.

4.3.3 Purifying the used water

Following presedimentation the water may be considered pure from the aspect of filterability. There could be two presedimentation stages applied, but this is not needed. In the water coming from the preliminary settling tank all substances to be removed may only be found in a dissolved state. The situation is totally similar to bank filtering. From a molecular aspect, the water of Danube contains the same elements as wastewater. Let us think of the case when wastewater gets into living water in an unpurified state. The only difference is the extent of dilution, that is in the concentration.

Thus, it is the question: whether the water can be purified by biological filtering or not.

The criterion of wastewater utilisation according to which energy output should be the maximum may be met if no sludge is used to water purification. In the pools with oxic-anoxic operation of traditional wastewater treatment the energy content of sludge necessarily decreases, thus reducing the extent of biogas output.

The degradation of nutrients needs a lot of air, whose method of introduction is not indifferent. Plate deep-aerators have such a great pressure demand because air is led to them in a very disadvantageous method, since it has to be made to get through activated sludge of high viscosity. The operation of blowers consumes lots of energy. Following pre-sedimentation, in the case of filterable pure water it is possible to replace blowers with fans.

This issue will be analysed below by means of using the technique of comparison. From this point on, general water treatment has to be discussed, and there is no point in separating drinking water purification and wastewater purification.

The quality of water to be purified deserves a more attention. The point to be discussed is what is to be removed from water. As it will be shown later, here the diffusion coefficient of organic materials will be decisive. How much is a question of totally different nature. The concentration measuring quantity (TOC, BDOC, COD, BOD_5) is generally identified as a measure of water quality. In the following this should be considered rather as a loading in relation to water purification, and as the extent of the recoverable energy content in case of incoming wastewater.

5. The proposal of application

The filter bed technology and the activated sludge technology may be compared by listing their advantages and disadvantages. The following table is though rather brief, it still points out at their important differences:

Table 5-1: Compare the technologies

	Filter bed technology (dimensioned on the basis of its similarity to bank filtering)	Activated sludge technology
Basic aim	Wastewater recycling	Wastewater treatment
Biogas production	The whole sludge quantity may be gasified.	Biogas yield is significantly lower as in the process of water purification the sludge becomes exhausted.
Necessary biological reactor space	About 20-fold smaller reactor space is needed.	Greater investment cost.
Biofilm carrier	This is needed and requires considerable additional costs.	The sludge itself performs this task.
Rinsing	Rinsing is needed, which involves the following: The filters should be rinsed - in the case of bank filtering twice yearly, - in wastewater recycling approx. every 2 days.	The task does not occur.
Mixing	It is not needed.	Mixing involves the use of electric energy.
Depth of the reactor space	Thickness of filtering layer is about 1.5 m.	The depth of the reactor space is great, 8 m.
Air feeding	From below, by low-power fan, through a 1.5 m thick filtering layer. The rinsing is air feeding as well.	The energy demand of blowers providing deep aeration is great.
Operation in winter	Bank filtering has a stable operation in winter as well, and therefore filter bed technology also does so.	Below 12°C nutrient degradation practically stops.
Operation	It needs a totally different thinking. Attention actually has to be paid to the rinsing of filters.	The flowing is continuous, the task of operation consists of interchanging oxic-anoxic spaces.
Input to technology by pumping water	It has to happen in the case of both technologies. Going through the technology is gravitational in both cases.	

And the alternative solution in figure:

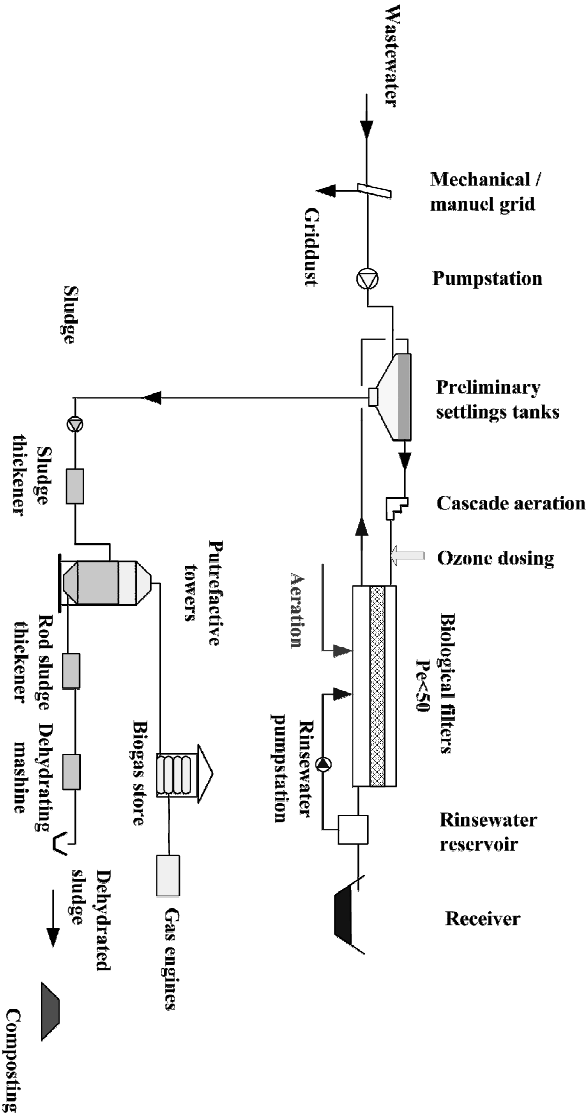


Figure 5-2: The new version of wastewater recycling in simple form

References

[1] Tolnai, B: Bevezetés a biológiai szűrés modellezésébe és méretezésébe (Introduction into the modeling and dimensioning of biological filtration). Patent application, National Patent Office of Hungary, Number: P0800635 / 2008.

[2] Tolnai, B.: Partiszűrés – a fertőtlenítés „weini” útja (Bank filtration – the Wein’s way of disinfection). MHT Vándorgyűlés, Baja, 2008.

[3] Tolnai, B. – Reichart O.: Az ivóvíz stabilitásának egy lehetséges mérőszáma (A possible measure of stability of drinking water quality). MHT Vándorgyűlés, Sopron, 2010.

[4] Tolnai, B.: Fertőtlenítés és fertőtlenítési rendszer (Disinfection and sanitation system). VízműPanoráma, Budapest, 2012.

[5] Tolnai, B..: Szennyvíztisztítás másképp, avagy a paradigmaváltás szükségessége (Wastewater treatment otherwise, or the need for a paradigm shift). ÖKOAQUA, Debrecen, 2012.

[6] Tolnai, B..: A biológiai szűrés alkalmazása (The use of biological filtration). MHT Vándorgyűlés, Kaposvár, 2012.

[7] Szirtes, Th.: Dimenzióanalízis és alkalmazott modellelmélet (Applied Dimensional Analysis and Modeling). Typotex Kiadó, Budapest. 2006.

[8] Sydsæter, K. –Hammond, P. I.: Matematika közgazdászoknak (Matematics for Economic Analysis, Chapter 8.4.). Aula Kiadó, Budapest 2000.

[9] Junker, Th..: A biológia története (Geschichte der Biologie, Die Wissenschaft vom Leben). Corvina Kiadó, Budapest 2007.

[10] Eckert, P. – Irmscher, R.: Over 130 years of experience with Riverbank Filtration in Düsseldorf. Journal of Water Supply 2006/4

[11] Jekel, I. – Grünheid,S.: Ist die Uferfiltration eine effektíve Barriere gegen organische Substanzen und Arzneimittelrückstände. GWF Wasser-Abwasser 148 (3007) Nr. 10.

Author

Béla Tolnai; tolnaibela@t-online.hu

Mechanical Engineer, Retired Operational Director of Waterworks of Budapest

Hope from sewage? Phages as an alternative to antibiotics

Johannes Wittmann

Leibniz-Institut DSMZ-Deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH

Abstract

Based on problems with multi-resistant bacteria causing infections in humans and animals, the search for alternatives to antibiotics is of current importance. Thus, the interest in bacteriophages for the therapeutical application to fight bacterial infections has increased during the last few years. Having been used successfully for this purpose in Georgia, Russia and also Western Europe for more than 30 years, during the Cold War bacteriophages were replaced by antibiotics and nearly forgotten in the Western World - till today.

1. What is a phage?

Bacteriophages (or phages) are viruses that specifically infect bacteria and can only replicate within their bacterial host cells. The spectrum of bacterial hosts is usually very narrow for each phage, therefore, phages are highly specific within one bacterial species or genus They only have two different principal components, a capsid consisting of different proteins that contains their genetic material (DNA or RNA, double- or single stranded)(Fig. 1A). Bacteriophages can be classified into different groups by their head and tail morphology, their nucleic acid and their genomic structure.

Most bacteriophages belong to the order *Caudovirales*, the tailed phages (Fig 1B). They can be further divided into *Myoviridae*, *Siphoviridae* and *Podoviridae*. Phages from the *Myoviridae* have relatively thick tails that can be contracted in order to inject their DNA from the head into the host cell. *Siphoviridae* have quite long and flexible tails that cannot be contracted, they represent the majority of the *Caudovirales*. Phages with small and stubby tails belong to the Podoviridae and are the smallest group of the *Caudovirales*. Furthermore there are also tailless and filamentous phages and more rare phages with "pleomorphic" structure like bottles or lemons the exotic structure of which reflecting a dependence to their fastidious bacterial hosts, and probably there are even more morphotypes that have not been found yet.

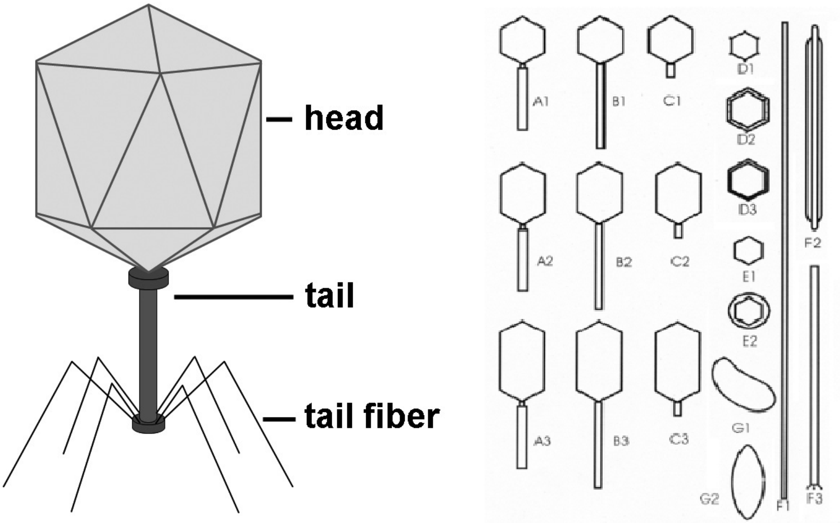


Fig.1: (A) Scheme of a typical T4-like phage (B) Morphological phage classification (Ackermann, 2003)

2. Bacteriophage life-cycles – understanding phages` impact on ecology and evolution

Apart from morphology and genomic structure, phages can also be divided into virulent and temperate phages according to their life-cycles (Fig. 2). This difference is of highly remarkable relevance for research in ecology and microenvironments, evolution research and other scientific fields of interest including the complex human “microbiome”. Even more because phages are the dominant living entities on earth, they are drivers of microbial evolution and therefore they have been shaping living systems and bio-communities on our planet.

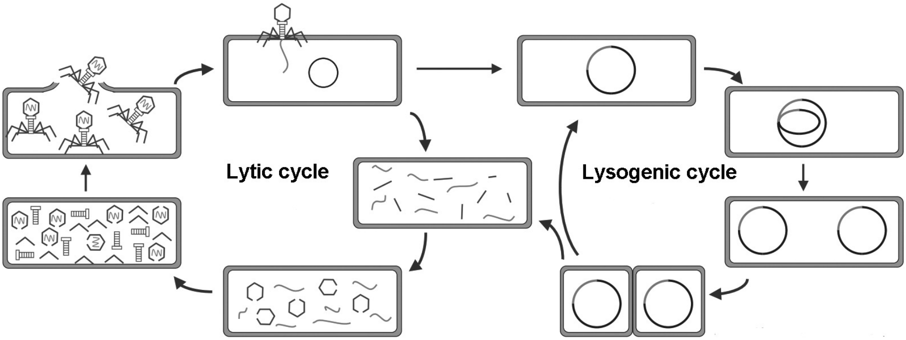


Fig. 2: Lytic and lysogenic life-cycle of bacteriophages (modified figure from Rohde and Sikorski, 2011)

The first step in both life-cycles is the adsorption of the phage to specific receptors on the bacterial surface (a highly specific process comparable to enzyme-substrate or “key-lock” specificity) and the following injection of their genetic material into the host cell. Virulent phages follow the lytic cycle; after injection of the DNA, so-called early genes are expressed that see to the shut-off and manipulation of the host metabolism for the production of new phage progeny. After replication of the phage genome and synthesis of head and tail structures, the phage DNA is packed into the capsid and the whole phage particle is assembled. The last step involves the lysis of bacterial cell by cell wall hydrolases and other enzymes that are forming holes in the bacterial cell wall and the release of the new bacteriophages into the environment follows (Fig. 3).

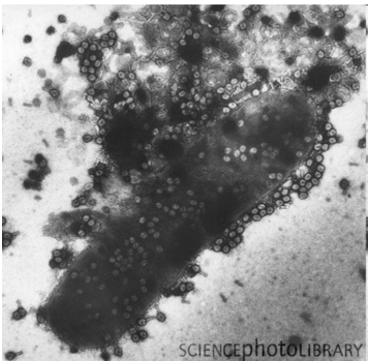


Fig. 3: Release of T4 phages from an *E. coli* cell (http://www.sciencephoto.com)

In contrast to that, during the lysogenic cycle the genome of temperate phages integrates as a prophage into the host genome at specific recombination sites and replicates with the host genome for many generations under the regulation of a repressor. These prophages are therefore “hidden” but can be induced by UV irradiation or certain chemicals that harm the host cell like mutagens. The phages are excised from the host genome and released to step into the lytic cycle causing proliferation of new phages. This demonstrates that such phages are able to switch between both life cycles. Logically, this fact causes a fundamentally different kind of potential by such phages compared to the lytic ones.

The role of bacteriophages for research and application has been recognised again during the past few years: obligately lytic phages can be useful “tools” where bacteria cause problems, especially such phages have a potential for application that cannot be overestimated – because they are reliably lytic. Temperate phages can integrate into the host’s genome as prophages and change between a lytic and a lysogenic cycle and can sometimes also change hosts as they can be transmitting vehicles of more or less long nucleic acid parts of the bacterial host including even complete host genes. Because of this “mobility” they bear a great potential of open research questions. Such phages are able to transmit parts of the host’s genome and hence, they are driving forces of biodiversification processes in all kinds of habitats, e.g. ocean water, sediments, soil, mud, all kinds of water reservoirs, extreme habitats and also of the human, animal or plant microbiomes. Phages and bacteria are co-existing in a balance, they develop in co-evolution. The number of phages depends on the availability of their hosts, this is one aspect of evolution dynamics. Natural systems like wind or water, which are mighty and constant forces on earth, carry bacteria and phages in huge amounts through the biosphere and mix continuously the gigantic gene pool of phage-bacteria systems. The earth has been designated a planet of phages: phages are the most abundant living entities, experts estimated their particle number at about 10^{31}, tenfold the number of bacteria. The human microbiome, the complete microbial community within and on the human body, bears about estimated 10^{14} bacteria, tenfold the number of cells of the body. But, also pathogenic bacteria can colonise this microbiome. Phages would often have the power to rescue life as they have the power to completely destroy the bacterial host at the location of the infection (hospital infections). This happens without known or described side effects and the phages themselves disappear as soon as their host is destroyed. Today, pathogenic bacteria that occur in the industrial livestock farming develop to be serious zoonotic disease-causing agents. Huge amounts of antibiotic substances are applied there, this includes also “prevention”. This has become one of the main causes of the vicious circle of multi-resistances against antibiotics. Also, plant-pathogenic bacteria could be eradicated by applying phages, without side effects. First products for agricultural application on fields against various phytopathogens like *Xanthomonas campestris* or

Clavibacter michiganensis are already available (AGRIPHAGE™, OMNILYTICS). Bacteria easily colonise food, especially on surfaces. *Listeria monocytogenes*, a dangerous pathogen, can contaminate cheese and other dairy products or sausages and other food, phages are already successfully used to prevent such food contamination in this field as well. Furthermore, phages can be used as indicators, e.g. for fecal bacteria in drinking water or for typing bacteria in new outbreak situations (e.g., phages against *Salmonella*). Even specific phage proteins like cell hydrolases are also already used as anti-microbial agents. All these examples demonstrate the huge range of possible phage application.

3. Advantages of phage application

Therapeutic application of phages has several advantages in comparison to treatment with antibiotics. First of all, bacteriophages are very specific, they only lyse their target bacteria, other members of the microflora are not affected, contrarily to antibiotics which often have a broad spectrum and destroy the majority of the microflora. It is known that this also causes harm to the human immune system that is partially located in the gut flora. Furthermore the phages are non-toxic to the eukaryotic cell. As natural components of the biosphere, we get into contact with them every day: on our skin, on food, etc., the human body should therefore be used to phages. Polish scientists at the Hirzfield Institute of Immunology and Experimental Therapy showed that, indeed, some people that have never been treated with phages already have antibodies against phages in their blood. Nevertheless it was only a minority and the levels of antibody production were only low, suggesting a successful treatment with phages if necessary. Moreover, in contrast to antibiotics which have to be taken regularly to keep the dosage on a high level, phages are self-replicating and self-limiting (see above). Their replication and propagation depends on the host organism, therefore only few applications and a small dose are enough for a successful elimination of the pathogen. After the host has disappeared, no sources for further propagation are at hand and the phage will also disappear after some time. Another important aspect is that phages -like their bacterial hosts- also constantly evolve and can adapt in situ to resistant bacteria strains. From the phages' point of view, it does not play any role whether or not their bacterial hosts are antibiotic-resistant or not. From the economic point of view, phage preparations are easy and inexpensive to produce and can be stored at 4°C or in a freeze-dried form for months or years without significant reduction in titer.

But before the production of a possible compound for application, there has to be done an intensive characterization of the isolated phages, including

- genome sequencing to exclude genes that indicate a lysogenic cycle or that might code for potentially toxic proteins
- host range analysis to identify and select phages with a broad host spectrum
- morphological analysis via transmission electron microscopy
- determination of optimal growth and “environmental” parameters (pH stability, temperature, etc.)

4. Phage therapy at the Eliava Institute in Tbilisi

Bacteriophages were first discovered independently by Frederick Twort and Felix d`Hérelle in 1915 and 1917, respectively. Their possible potential for the treatment of different infectious disease was immediately recognized. Together with George Eliava, Felix d`Hérelle founded the Eliava Institute in Tbilisi, Georgia, where phage therapy has been further developed and performed till today. Till 1941, when antibiotics and their potential to fight bacterial infections were discovered, a lot of research on phage biology and phage therapy was done also in Western Europe and the USA. Due to the barriers of the Cold War and the success of antibiotics, phage therapy did not seem to be of great interest in the Western world any more. In Russia and Georgia scientists continued to investigate phages and proceeded in the development of new compounds and techniques. That is why professional phage therapy based on a great number of empiric success stories is only approved in Russia and Georgia at the Eliava Institute today.

Fig. 4: A defined bacteriophage cocktail, BFC-1 against *Pseudomonas aeruginosa* and its application on an infected burn wound (from: Merabishvili, M., et al. (2009) Quality-controlled small-scale production of a well-defined bacteriophage cocktail for use in human clinical trials. *PLoS ONE* 4: e4944)

Patients from all over the world are currently treated with bacteriophages to fight bacterial infections that do not respond to conventional antibiotics any more. Different compounds against various bacterial pathogens and for different forms of application can be received in pharmacies or directly at the institute, including eye drops, sprays or pills (Fig. 4).

5. Current research on bacteriophages at the DSMZ

The current research project deals with the diversity of phage-host interactions in clinical and environmental strains of bacteria of the order *Burkholderiales*, especially in the genus *Achromobacter*. The number of multiple antibiotic resistant strains is dramatically increasing and there is serious concern in hospitals, especially. This project deals with the use of bacteriophages against these infectious bacteria as a promising alternative to antibiotics. Thereby two different research lines are followed, both representing aspects of fundamental research aiming at fully understanding the role of the *Achromobacter* strains in the context with the diversity of specific phages. The first line deals with the isolation and further characterisation of new bacteriophages in order to investigate their ability to lyse multiple resistant strains of the pathogen for putative practical use. The second line analyses a possible role of these bacteriophages in evolution of this species as bacteriophages might act as vehicles for gene transfer by transduction or by recombination in cases of lysogeny.

5.1 *Achromobacter xylosoxidans* as an emerging opportunistic pathogen

Achromobacter xylosoxidans is a nonfermenting, oxidase- and catalase-positive, motile gram-negative rod that can be found widely distributed in natural environments, mainly in moist soil or water sources like well water or swimming pools. Its genome reveals genes associated with pathogenesis, toxin production and antibiotic resistances. Hence, apart from its role as an environmental organism, *A. xylosoxidans* has been recognized during the last years as an emerging nosocomial pathogen. For example, in cystic fibrosis it has become even more prominent than members of the *Burkholderia cepacia* complex. It potentially causes a wide range of different human infections also in non-CF patients and is an emerging threat for immunocompromised patients as well. Several epidemiological studies also showed that *A. xylosoxidans* is able to survive in uncommon habitats, such as the antisept chlorhexidine, or on inanimate surfaces in hospitals. Furthermore, there are reports about outbreaks of infections caused by contaminated dialysis fluids, contrast solutions or ultrasound gels, emphasizing its potential as a nosocomially spread opportunistic pathogen. In sum, *A. xylosoxidans* has become a serious human pathogen that needs appropriate clinical control.

Typically, since the discovery of Penicillin by Alexander Fleming microbial infections have been treated mainly by antibiotics. However, reports on occurring and dramatically developing resistances against antibiotics also in *A. xylosoxidans* mirror the increasing weakness of antibiotics and underline the need to find alternatives to fight against this organism. Several beta-lactamases and resistances against aminoglycosides have been described for *A. xylosoxidans*. Nosocomially acquired bacteria can cause dangerous health threats for individuals or even outbreaks if associated with multidrug-resistances.

Phages offer some advantages compared to antibiotic therapies: they are highly specific against their target bacteria, self-reproducing at the focus of bacterial accumulation without disturbing the obligate bacterial flora and therefore, without the side effects known for antibiotic drugs. However, until now, phages for *A. xylosoxidans* are hardly known, and the available literature is scarce and old. It is unclear if a substantial diversity of phages against *A. xylosoxidans* exists at all and if they potentially could serve as therapeutic phages against this pathogen. Therefore, the leading approach of our investigations was to discover and describe the phage diversity for this species.

5.2 Isolation of new bacteriophages against *Achromobacter xylosoxidans*

Since *Achromobacter xylosoxidans* is an ubiquitous bacterium in water and soil, and phages are abundant in a high concentration as well (one drop of seawater contains ~50 million phages per ml, even higher titers in soil samples), samples from waste water treatment plants were assumed to be a promising source for the isolation of new phages against this species. New phages were obtained by standard enrichment techniques (Fig. 5).

Different centrifugation and filtration steps were used to separate already existing bacteriophages from dirt particles and bacteria. For enrichment of suitable bacteriophages, cultures of possible bacterial host strains were mixed with nutrient solution and filtered samples. After incubation and removal of bacteria, aliquots of the filtrates were tested in a so called plaque assay on agar plates for phages. Filtrates that contained bacteriophages against *Achromobacter xylosidans* could be identified by the presence of plaques on the agar plates after further incubation. Bacterial cells usually form bacterial lawns on the agar plate if appropriately inoculated.

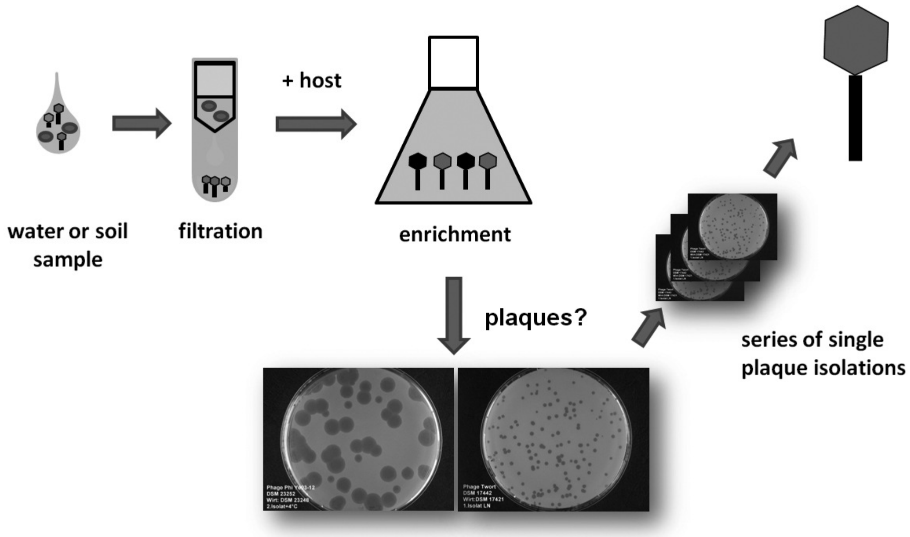


Fig. 5: Enrichment, detection and purification of bacteriophages from environmental samples

If a phage is able to adsorb to a suitable host cell, it infects this cell and produces new phages resulting in the lysis of the bacterial cell. Zones where a phage was able to infect and lyse its bacterial host look like small, mostly transparent holes in the bacterial lawn and are called plaques. Those plaques can differ in size and turbidity, depending on the phage. Single plaques were then further purified by dilution steps and repeated single plaque isolation. Altogether, 32 different bacteriophages against *Achromobacter xylosoxidans* could be isolated from waste water and soil samples.

5.3 Characterization of different bacteriophages

Preliminary characterization was done by host range analysis, DNA restriction digestion and morphological analysis by electron microscopy. After analysis of this data, it could be shown that there is a broad diversity among the morphotypes of the isolated *Achromobacter* phages (Fig. 6).

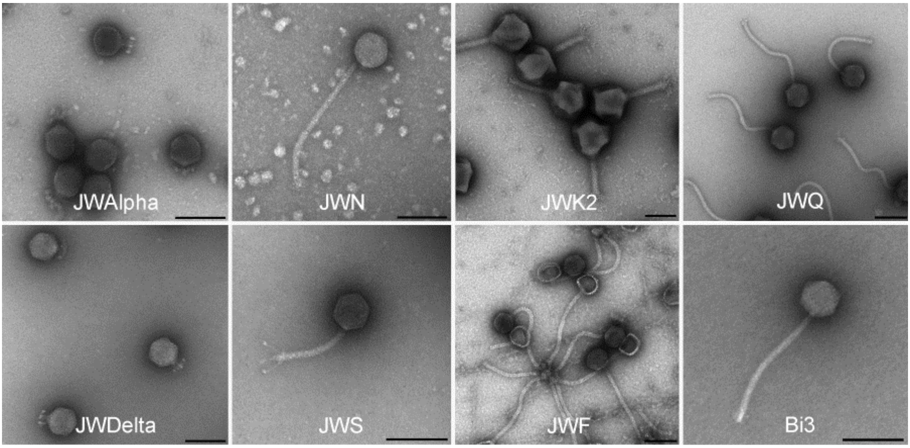


Fig. 6: Electron micrographs of several *Achromobacter* phages from different waste water treatment plants (Wittmann, et al., under review)

Members of all families of the *Caudovirales* could be identified so far, with the *Siphoviridae* (e.g. phages JWQ and JWS) as the most prominent group.

Host range analysis revealed several phages with a relatively broad host spectrum, making them interesting candidates for further characterization. Some of these phage genomes were already sequenced using PacBio RS and further analyzed in detail with bioinformatic tools to get the all the genetic information for future experiments. The genome sequences also revealed a broad diversity with some so far unknown genomic structures. Two podoviruses, JWAlpha and JWDelta, were isolated from two different waste water treatment plants with a geographical distance of about 250 km that surprisingly show high morphological similarities, their genomic sequences showed high homologies to N4-like phages that form a group with only 14 members so far known worldwide.

5.4 Phage Trapper Project

Without doubt, the useful potential of phages is quite high and therefore, broad phage diversity is an important aim of the DSMZ. Even more because there are only very few culture collections in Europe that have phage expertise. It is also fundamental for research projects to establish a big pool of phages and to maintain them authentic and stable for future generations. Thus, the DSMZ started the Phage Trapper Project (http://www.dsmz.de/research/microorganisms/projects/phage-trapper-project.html) in cooperation with different German universities. In this project students learn how to isolate and characterize new phages against various bacteria. Working on this project a lot of people from different places can contribute to the broad diversity of this phage collection. The first student who attended was able to find 30 phages against 19 different bacterial species in 1 sample.

Author

Dr. Johannes Wittmann

Leibniz-Institut DSMZ-Deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH

Inhoffenstraße 7 B

38124 Braunschweig

Germany

Tel. ++49-531-2616-220

Fax ++49-531-2616-418

jow12@dsmz.de

http://www.dsmz.de

Elimination of Microcystin-LR and selected pharmaceutical residuals using biologically active filters

Xin Wu

Institute of Sanitary and Environmental Engineering, Technische Universität Braunschweig

Abstract

Microcystin-LR (MC-LR) and pharmaceutical residues are new emerging pollutants posing hazardous impact on the aquatic system and human beings. Compared to treatment processes e.g. ozonation, adsorption with activated carbon or reverse osmosis, the biofiltration process excels in its low environmental impact. The objective of this study is to investigate the removal of MC-LR and pharmaceutical residues by using biologically active filters. Three different types of filter materials were investigated, activated carbon, lignite and basalt. Experimental results indicated that higher removal efficiencies for both groups of substances were achieved in GAC and lignite filters. High removal rates up to 30 and 60 µg MC-LR/L•h were respectively yielded by the lignite and GAC filters. We were also able to develop two models describing the removal of MC-LR by lignite- and GAC filters as reactions of first order with satisfactory accuracy. Furthermore, costs calculations suggest that the biofiltration process can be an economically competitive option to adsorption processes applied as the advanced treatment in a waste water treatment plant.

Keywords: MC-LR; pharmaceutical residues; biofilter; granular activated carbon; lignite; model; costs

1. Introduction

A number of new emerging pollutants have been detected in different matrices of our environmental system successively over the last decades. Due to their potential hazardous long-term impact on the aquatic system and human beings, a number of research and practical works have been carried out focusing on their elimination from the drinking water or the wastewater. The target substances of this study, MC-LR and pharmaceutical residues are two groups of emerging pollutants of major concern respectively in the drinking water and the wastewater. MC-LR is considered the most toxic compound of the family of cyanotoxine, a group of toxine produced by cyanobacteria, also known as blue algae. MC-LR inhibits the activities of protein phosphatase in the liver and can cause severe liver damages. By obtaining drinking water from sources contaminated with algae blooms, a practice not unusual in developing countries, the public health is put at great risk. It is also based on the public health risks that the WHO released a guideline value of 1 µg/L for the MC-LR concentration in drinking water. Pharmaceutical residues, on the other hand, present itself mainly as a new problem in the wastewater treatment. Since their detection in the aquatic systems in the 90^{th} and the discovery of several adverse effects, there has been a growing effort to establish advanced treatment processes in Germany to remove them from the wastewater, thus minimizing the amount entering the surface water and ground water. The objective of this study is to investigate the elimination of MC-LR and pharmaceutical residues diclofenac, ibuprofen, carbamazepine and sulfamethoxazole using biologically active filters. Compared to treatment processes e.g. ozonation, adsorption with activated carbon or reverse osmosis, the biofiltration process excels in the low material and energetic input, resulting in a low environmental impact. Previous investigations have shown that MC-LR is likely to be biologically degraded in slow sand filters (Grützmacher et al., 2002, 2006; Bourne et al., 2006; Ho et al., 2006a, 2006b, 2007; Sá et al., 2006). Several recent research works have also indicted the possibility of applying biologically active filters as an advanced treatment of the waste water to eliminate pharmaceutical residues (Reungoat et al., 2011; Weemaes et al., 2011; Meda, 2012) In this study, the efficiencies of three different biofilters using granular activated carbon (GAC), lignite and basalt as filter materials were studied. The influences of the influent concentration and the empty bed contact time (EBCT) on the removal of MC-LR were investigated, with the aim to develop mathematical descriptions of the removal process in biofilters. Furthermore, the costs of the biofiltration process together with two adsorption processes using powered activated carbon (PAC) and GAC serving as the advanced treatment stage for a wastewater treatment plant (WWTP) were calculated and compared. The aim is to reveal under which circumstances the biofiltration process can be applied as an economically competitive alternative to the adsorption processes.

2. Experimental methods

2.1 Materials and reagents

Two adsorptive filter materials, GAC and lignite and one non-adsorptive filter material, basalt were employed in the experiments. The particle sizes of the three materials were 1.7 – 3.3 mm (GAC), 1.25 – 5 mm (lignite) and 2 – 5 mm (basalt). Three different types of water were used in the experiments, effluent from the WWTP Braunschweig, river water and artificial fresh water (distilled water with addition of salts).

2.2 Experimental set-up

Approximately 1 Litre of each filter material was packed in a glass cylinder (diameter 10 cm, height 12 cm). The experimental set up is presented in Figure 1. Filters could be operated in two modes, batch mode and continuous-flow mode. Temperature in the lab was kept at 20 + 1°C.

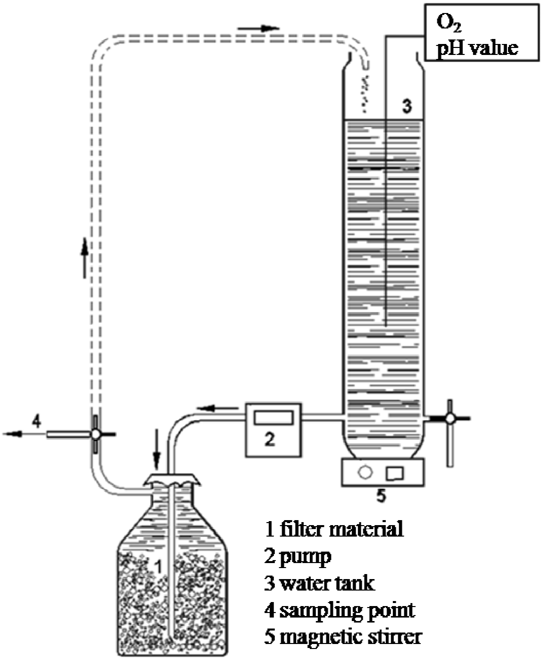


Figure 1: Schematic set-up of the laboratory experiments

2.3 Conditioning of the filters

The filter materials GAC and lignite were submerged in the effluent of the WWTP Braunschweig for two months to deplete their physical adsorption capacity and develop biological activities. During this time, basalt was fed with the effluent of the WWTP in the lab to establish biological activities.

3. Removal efficiencies of MC-LR and pharmaceutical residues

The removal rates of MC-LR and the four selected pharmaceuticals are respectively listed in Table 1, 2 and 3. The removal efficiencies of MC-LR are demonstrated at both different EBCTs and different filter loads.

Both GAC and lignite filters remove MC-LR and selected pharmaceuticals at high efficiencies. The lignite filter reaches removal efficiencies of steadily over 90 % for both groups of target substances, even at filter loads as high as 60 µg/L·h for MC-LR. The GAC filter reaches high removal efficiencies of over 70 % for MC-LR at a filter load of less than 30 µg/L·h. At higher filter loads, the removal efficiency decreases. The removal efficiencies of the four pharmaceuticals by the GAC filter are steadily at over 80%. It should however be mentioned, that the removal efficiencies of pharmaceuticals are achieved at much lower filter loads compared to those of MC-LR. The removal efficiencies achieved by the basalt filter are significantly lower than by both GAC and lignite filters. At a filter load of above 20 µg MC-LR/L·h, the removal efficiencies already decrease to lower than 30%. The basalt filter also proves incapable of eliminating carbamazepine and sulfamethoxazole. The high efficiencies demonstrated by The GAC and lignite filters are believed to be connected to their large specific surface areas, which provide microorganism with more favorable conditions for colonization. Additionally, although both filter materials were fully adapted and conditioned, there could still be a slight remaining adsorption capacity which assisted in eliminating substances at low concentrations of micrograms per liter.

Table 1: Removal efficiencies of MC-LR at different EBCTs, MC-LR influent concentrations: 5 - 40 µg/L

	Removal efficiencies ηMC-LR (%)		
	EBCT = 2 h	EBCT = 1 h	EBCT = 0,5 h
GAC	88 - 93	70 - 82	50 - 80
lignite	100	95 - 100	90 -100
basalt	50 - 80	12 -58	20 - 40

Table 2: Removal efficiencies of MC-LR at different filter loads, MC-LR influent concentrations: 5 - 40 µg/L

	Removal efficiencies ηMC-LR (%)		
	Filter load 0 – 20 µg/L·h	Filter load 20 – 40 µg/L·h	Filter load 40 – 60 µg/L·h
GAC	70 - 93	63 - 77	50 - 52
lignite	98 - 100	93 - 98	92 - 93
basalt	33 - 79	12 - 33	-

Table 3: Removal efficiencies of diclofenac, ibuprofen, carbamazepine and sulfamethoxazole at different filter loads, influent concentrations of a single compound: 2 – 15 µg/L

	Removal efficiencies in % (Filter load in µg/L·h)			
	diclofenac	ibuprofen	carbamazepine	sulfamethoxazole
GAC	84 - 100 (≤ 10.8)	80 – 100 (≤ 4.6)	80 - 100 (≤ 8.1)	78 -100 (≤ 4.6)
lignite	80 – 100 (≤ 1.2)	96 – 100 (≤ 1.2)	91 – 100 (≤ 0,6)	97 – 100 (≤ 1,2)
basalt	6 – 72 (≤ 1.5)	74 – 100 (≤ 1.2)	negative	negative

4. Model description for the removal of MC-LR

The removal of MC-LR by both GAC and lignite filters follows a clear pattern. The removal rates increase with the increasing influent concentration at a constant EBCT, as can be seen in Figure 2. This pattern can also be expressed as the increase of removal rates with the increasing filter load, which is the quotient of the influent concentration and the corresponding EBCT mathematically and reflects therefore the combined influence of both parameters (Figure 2). Both correlations suggest that the elimination rate of MC-LR is dependent on its concentration or supply rate. This kind of dependency of the substrate reaction rate on the substrate supply rate can be found in both the Michaelis-Menten-kinetics describing the enzymatic reaction and the Langmuir adsorption model describing the adsorption kinetics. Since the biological degradation is likely to play the major role in the filtration process with adsorption as a possible assisting mechanism, this dependency of the removal rates on the substrate concentration or supply rate can be plausibly explained by both mechanisms mentioned above. Whereas the removal of MC-LR by the lignite filter seems to fit into a first-order reaction, the removal rates of MC-LR by the GAC filter at high filter load do not increase as fast as at low ranges, suggesting a reaction between zero- and first-order.

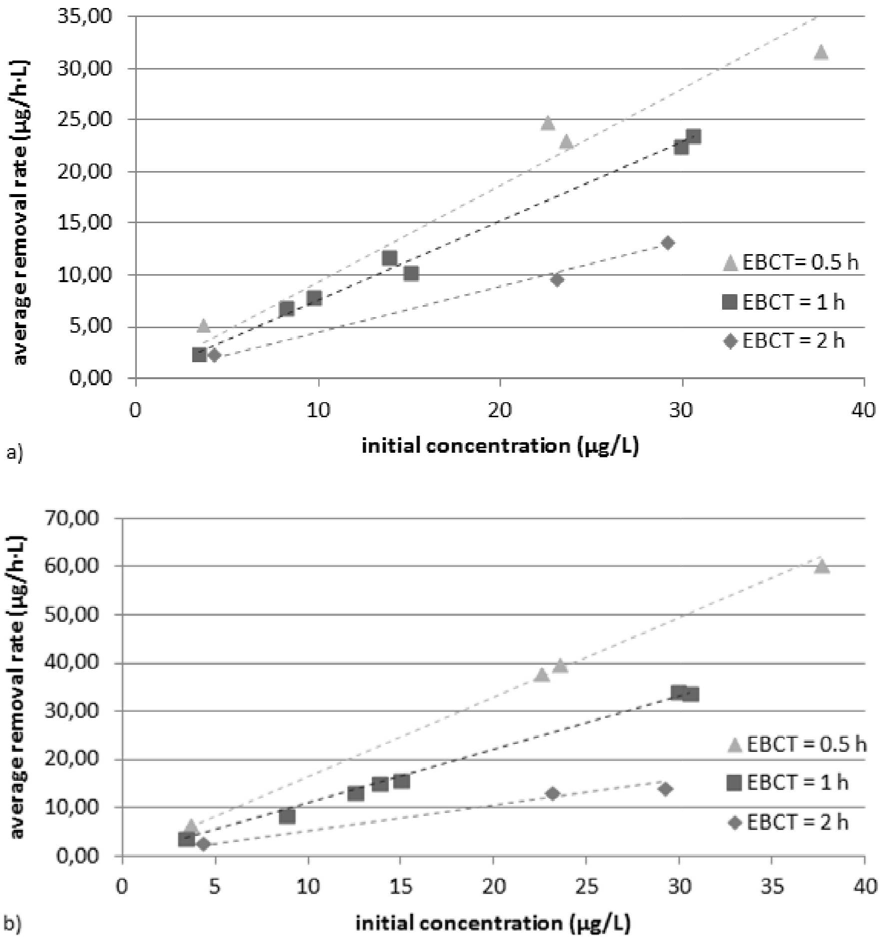


Figure 2: Average removal rates of MC-LR at different initial MC-LR-concentrations and different EBCTs in a) GAC filter and b) lignite filter

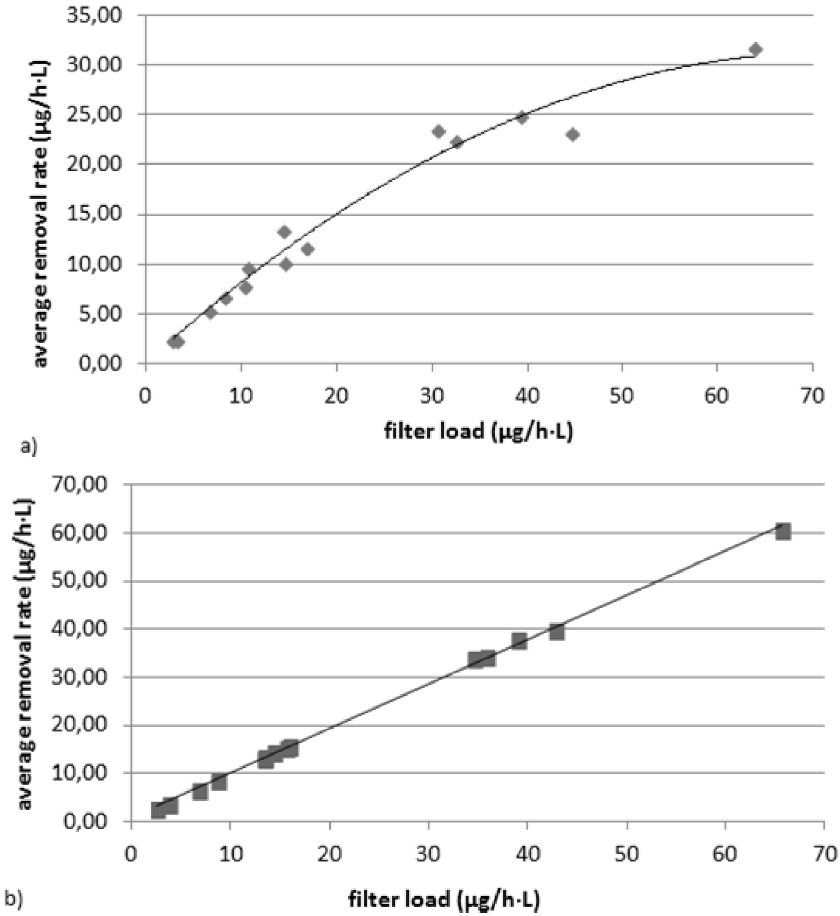


Figure 3: Average removal rates of MC-LR at different filter loads in a) GAC filter and b) lignite filter

By combining the reaction kinetic between zero- and first-order

$$v = v_{max} \cdot \frac{C}{k+C}$$

and a plug-flow model

$$\frac{\partial C}{\partial t} = -\frac{Q}{A}\frac{\partial C}{\partial H} + v$$

with	v	reaction rate [µg/L·h]
	v_{max}	maximal reaction rate [µg/L·h]
	c	substrate concentration [µg/L]
	k	constant [µg/L]
	t	time [h]
	H	distance in the vertical direction of the filter [cm]

we were able to develop two models to describe and predict the removal of MC-LR by lignite- and GAC filters as a function of the MC-LR concentration in the influent and the EBCT.

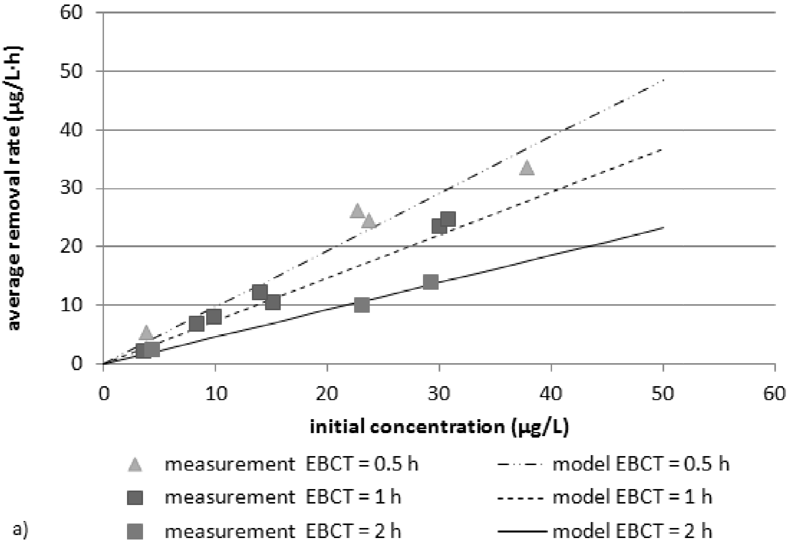
GAC-filter:

$$C_0 = e^{\left(1{,}33 \cdot \frac{V}{Q}\right)} \cdot C_e$$

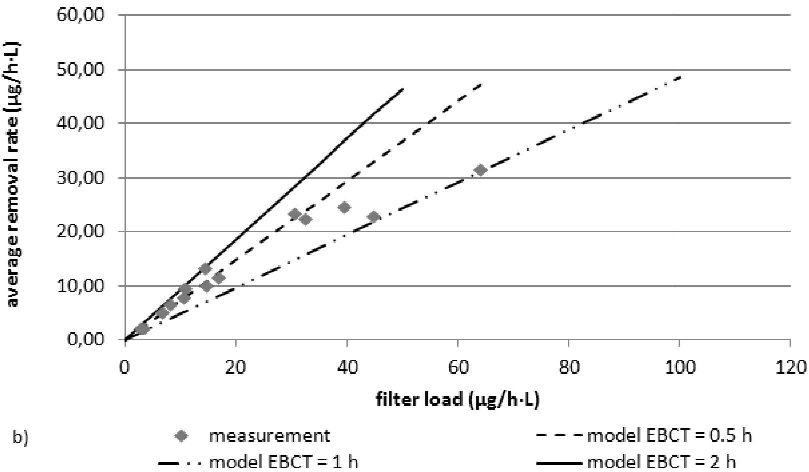
Lignite-filter:

$$C_0 = e^{\left(4{,}47 \cdot \frac{V}{Q}\right)} \cdot C_e$$

The model calculated removal rates are demonstrated in Figure 4 and 5 as a function of the initial concentrations and EBCTs or as a function of the filter loads. In the comparison with the experimentally measured data, both models reflect experimental result in both filters with sufficient accuracy. As the model predictions reveal, the elimination of MC-LR in both GAC and lignite filters are rather influenced by the influent concentration of MC-LR and the EBCT separately, instead of solely by the filter load as the combination of both parameters. This can be best seen in Figure 4 b), in which the removal rate can be rather different at a certain filter load if the EBCT varies. The separate influence of influent concentration and EBCT also applies for the lignite filter. However, at a certain given filter load, the alteration of EBCT between 0.5 and 2 h affects the removal rate only insignificantly. This can be plausibly explained by the observed high removal rates in the lignite filter which means it can be operated at a low EBCT without having a negative influence on the efficiency.



a)



b)

Figure 4: Comparison between measured and model predicted removal rates in the GAC-filter a) at different initial concentrations and EBCTs or b) at different filter loads

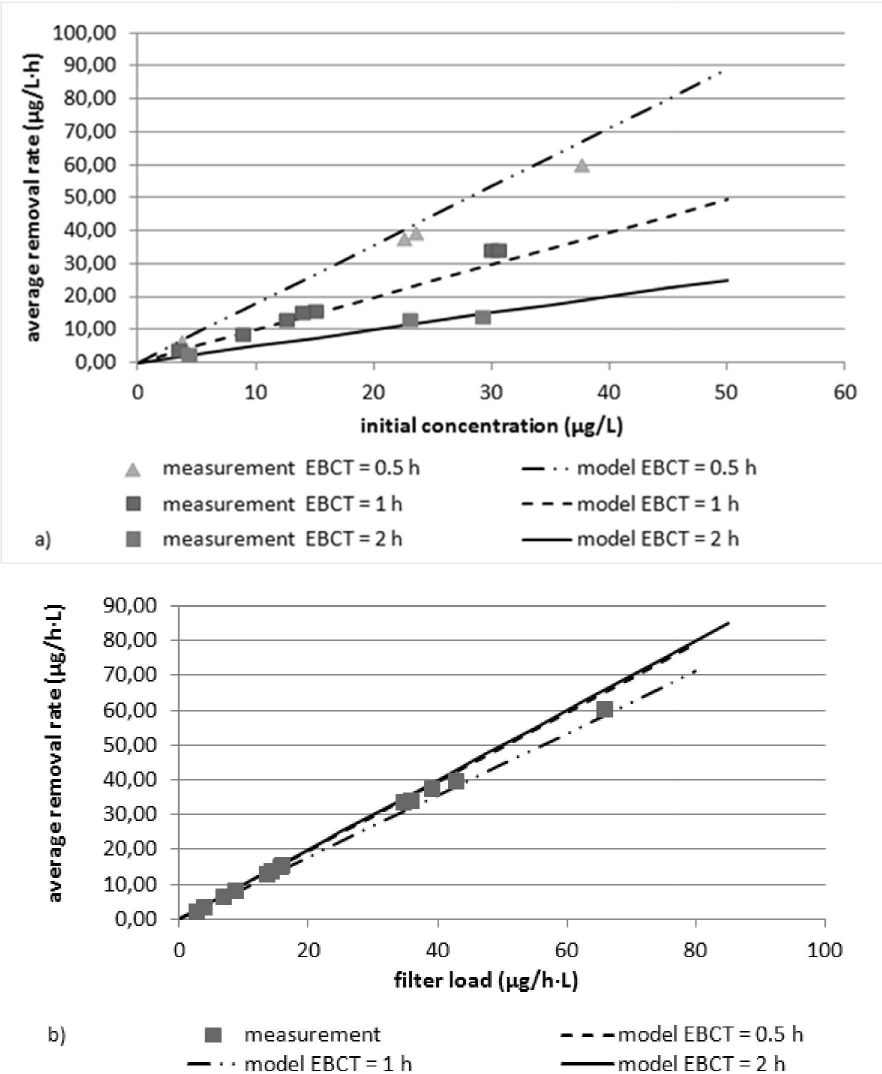


Figure 5: Comparison between measured and model predicted removal rates in the lignite filter a) at different initial concentrations and EBCTs or b) at different filter loads

5. Economical aspects

The economical aspects are an inevitable part of the decision making process, when an advanced treatment process should be chosen and implemented to remove emerging pollutants in an existing plant. Since such advanced treatment stages specifically for the elimination of MC-LR are still absent in the practice of the drinking water treatment, whereas many WWTPs have already set up or are planning such additional treatment processes to eliminate pharmaceutical residues from the wastewater, the following economical comparison are carried for removing pharmaceutical residues from the wastewater with additional treatment stages.

We calculated and compared the costs of three treatment processes, two adsorption processes with respectively PAC and GAC and the biofiltration process using GAC as filter material (BAC). The PAC treatment process is the most widely implemented process currently in WWTPs in Germany and presents itself as a good reference. The comparison between GAC and BAC processes should reveal under which circumstances the operation of BAC filters as an extended use of GAC filters may prove feasible.

Relevant operational parameters are chosen as follows:

PAC-dosage:	10 or 20 mg/L
EBCT of the GAC filter:	75, 30 and 15 min
Exchange volume of the GAC filter:	9000
EBCT of the GAC filter:	2 h and 75 min
Exchange volume of the BAC filter:	20,000 and 40,000

The costs calculations are carried out under further relevant assumptions:

expected life time:	construction:	30 a
	machine	15 a
	EMSR:	10 a
interest:		3 %
energy consumption:	PAC process	0.04 kWh/m³
	GAC and BAC process	0.025 kWh/m³
energy price:		0.15 €/kWh
salary per personal:		50,000 €/a
annual maintenance:	construction:	1% of the capital costs

	machine	4% of the capital costs
	EMSR:	2% of the capital costs
material:	PAC:	1,100 €/ton
	GAC:	1,100 €/ton
	coagulant:	2,300 €/ ton Al
	coagulation aids:	1,300 €/ ton

The annual costs of the BAC process are compared respectively with the PAC and GAC processes in Figure 6 and 7 for WWTPs with a population equivalent (PI) up to 400,000. The selection of the EBCT obviously affects the annual costs of the BAC process magnificently. The choice of an EBCT of 2 h results in such high annual costs that the BAC process will be of complete economical disadvantage compared to the PAC process. The BAC process can however present itself as economically competitive to the PAC process, when the BAC is designed with a shorter EBCT of 75 min or even less. A high achievable exchange volume will add an additional advantage to the BAC process. If the BAC can be operated up to an exchange volume of 40,000 instead of 20,000, the annual costs can be reduced by approx. 15 % for a WWTP with a PI of 400,000. Generally speaking, an economical advantage of the BAC process compared to the PAC process can be given, if the BAC facility can be operated at an EBCT of 75 min or less and an exchange volume of 40,000 or more. As compared with the GAC process, the choice of the EBCT in the GAC process clearly has a considerable impact on the annual costs as well. The BAC process will be economically of clear advantage, when compared to a GAC plant operated with an EBCT of 75 min or more. The BAC process will however still be an economically competitive option to the GAC process operated with an EBCT of 30 or 15 min, if the BAC process itself can be operated at an EBCT of 75 min or less. For WWTPs with a PI of fewer than 100,000, the BAC process presents itself generally as the economically competitive or favorable option compared to both PAC and GAC processes.

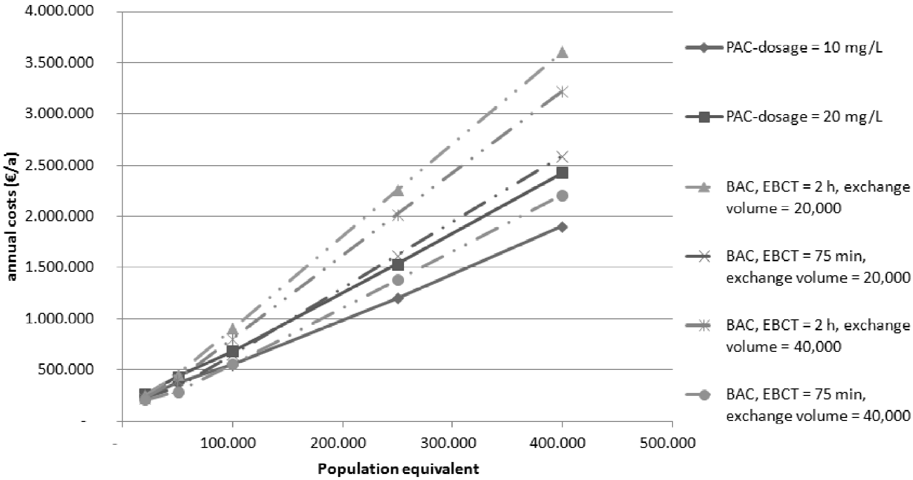


Figure 6: Annual costs of PAC and BAC processes implemented as advanced treatment stages for the removal of pharmaceutical residues from the wastewater

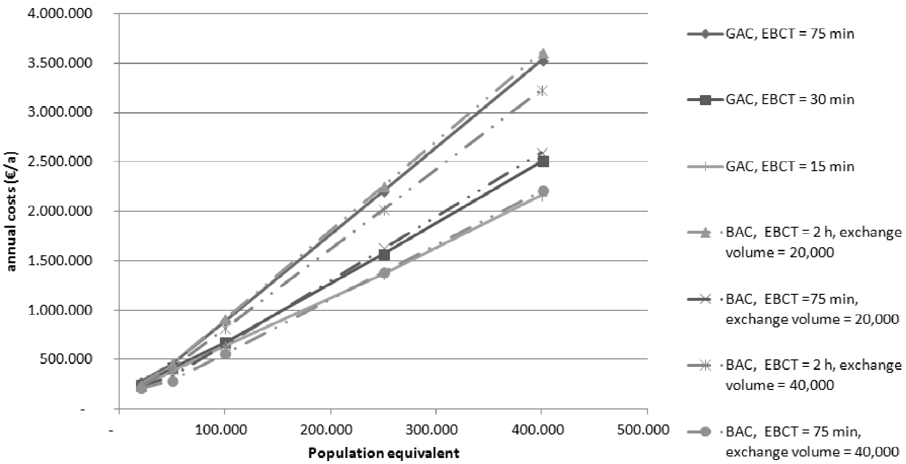


Figure 7: Annual costs of GAC and BAC processes implemented as advanced treatment stages for the removal of pharmaceutical residues from the wastewater

6. Conclusion

The experimental results indicate that the biofiltration is a promising process option for the removal of MC-LR and pharmaceutical residues. Of the three filter materials investigated in the experiments, lignite and GAC filters showed considerably higher elimination efficiencies for both groups of substances than basalt and prove to be the more suitable filter materials. The elimination rates of MC-LR increase at increasing initial substrate concentrations or filter loads, correlations which we were able to describe by two models of first-order reaction with sufficient accuracy. As the model predictions reveal, the elimination of MC-LR in both GAC and lignite filters are rather influenced by the influent concentration of MC-LR and the EBCT separately, instead of solely by the filter load as the combination of both parameters. The comparison of annual costs between BAC, PAC and GAC processes serving as an advanced treatment stage for the removal of pharmaceutical residues in a WWTP indicate, that the BAC process can be an economically competitive or even favorable option to both PAC and GAC processes, if the BAC process can be operated at a low EBCT and a high exchange volume.

References

Bourne, D.G., Blakeley, R.L., Riddles, P., Jones, G.J. (2006). Biodegradation of the cyanobacterial toxin microcystin LR in natural water and biologically active slow sand filters. Water Research, 40, 1294-1302

Grützmacher, G., Böttcher, G., Chorus, I., Bartel, H. (2002) Removal of microcystin by slow sand filtration. Environ Toxicol., 17(4) 386-394.

Grützmacher, G., Wessel, G., Chorus, I., Bartel, H. (2006). Removal of cyanobacterial toxins (microcystins) during slow sand and bank filtration. In: Recent Progress in slow sand and alternative biofiltration processes, R. Gimbel (ed.), London, IWA Publishing, pp. 171-177

Ho, L., Meyn, T., Keegan, A., Hoefel, D., Brookes, J., Saint, C.P., Newcombe, G. (2006a). Bacterial degradation of microcystin toxins within a biologically active sand filter. Water Research, 40, 768-774

Ho, L., Hoefel, D., Meyn, T., Saint, C.P., Newcombe, G. (2006b). Biofiltration of microcystin toxins: an Australian perspective. In: Recent Progress in slow sand and alternative biofiltration processes, R. Gimbel (ed.), London, IWA Publishing, pp. 162-170

Meda, A. (2012) Einsatz von Biofiltern für die Wasser- und Nährstoffwiederverwendung und für die weitergehende Abwasserreinigug zur Spurenstoffentfernung. (Schriftreihe 217). Herausgeber: Verein zur Förderung des Instituts IWAR der TU Darmstadt e.V.

Reungoat, J. Escher, B.I., Macova, M., Keller, J. (2011) Biofiltration of wastewater treatment plant effluent: Effective removal of pharmaceuticals and personal care products and reduction of toxicity. Water Res. 45, 2751-62.

Sá, J.C., Brandão, C.C.S., (2006). Removal of microcystis aeruginosa and microcystins by slow sand filtration: a pilot scale study. In: Gimbel R, ed. Recent Progress in slow sand and alternative biofiltration processes. London, IWA Publishing, pp. 178-187

Weemaes, M., Fink, G., Lachmund, C., Magdeburg, A., Stalter, D., Thoeye, C., De Gueldre, G., Van De Steene, B. (2011) Removal of micropollutants in WWTP effluent by biological assisted membrane carbon filtration (BioMAC). Water Sci Technol. 63(1), 72-9

Author

Xin Wu

Institut für Siedlungswasserwirtschaft, Technische Universität Braunschweig, Germany

Pockelsstrasse 2a, Braunschweig, 38106, Germany

(E-mail: wu.xin@tu-braunschweig.de)

Options for the use of recovered N- and P-fertiliser in agriculture

Daniel Klein

Institute of Sanitary and Environmental Engineering, TU Braunschweig

1. Introduction

The global demand of agricultural products is steadily growing, as well as the demand of fertiliser. As a result, the fertiliser market is very volatile. After an enormous increase of prices in 2008, prices dropped over 50%. Today, fertiliser prices are more or less stable on a high level (VHE 2013). Given the growing world population – whose food supply will mainly depend on the specific harvest per hectare and thus, fertiliser – it has to be expected that fertiliser prices will still rise.

Given this global context, many research projects during the last 10 years have focused on the recovery of nutrients from wastewater streams. In case of phosphorus, recovery is crucial, because it is an essential resource whose reserves will last for some 100 years maximum (Elsner 2008). The resources of nitrogen are unlimited, but given the high prices of mineral N-fertiliser and the high energy demand of its production, the recovery of nitrogen is also reasonable from an economic and ecologic perspective.

The most self-evident option to use recovered nutrients is the use as fertiliser. The following paper focuses on the adaptation of nutrient production (on wastewater treatment plants) and nutrient demand (of agriculture) and the economic aspects of agricultural reuse.

2. Nutrient recovery

2.1 Phosphorus recovery

Many options have been researched to recover P from wastewater. Depending on the specific wastewater stream, up to 90% of the total P can be recovered. Table 1 gives an overview of the most common sites/streams of phosphorus recovery with their specific properties. Information is taken from Pinnekamp et al (2005), UBA (2007), Herrmann (2009) and Egle & Reichel (2012) who also give further information about phosphorus recovery options.

Table 1: Properties of various locations of P-recovery in a wastewater treatment plant

Location/ Stream	Recovery ratio/recovery potential	Remarks
WWTP (wastewater treatment plant) effluent	low; max. 10-15% of total P-influent on standard WWTPs	Recovery up to 50% possible, if no P-removal on WWTP. Stream with very low concentrations
Sludge liquor	medium. Process water of sludge dewatering contains up to 20% of total P-influent	Lower potential, if chemical P-precipitation. High P-concentrations
Digested sludge	high (up to 80-90%), depending on pre-treatment/disintegration of sludge	High P-concentrations
Dewatered sludge	medium-high. Up to 90% of P are fixed in sludge, but 100% solubilisation of P not possible	
Ash	high. Up to 90% of P are fixed in sludge; compared to dewatered sludge, 100% solubilisation from ashes almost possible	Complex process (Incineration, solubilisation, removal of heavy metals...) Very high P-concentrations

Some technologies have yet been transferred to full-scale applications, but generally, the implantation is not yet economically feasible. It can be expected that within the next 10-15 years, some of the recovery methods will be feasible due to technological developments (Sartorius 2011).

2.2 Nitrogen recovery

In contrast to P, nitrogen treatment techniques are not yet implemented with the aim to recover nitrogen, but only as a separate treatment for nitrogen elimination. Ammonia stripping is a state-of-the-art method to eliminate NH_3 as DAS (Di-ammonium sulphate) from highly concentrated wastewater streams such as sludge liquor (Jardin et al 2005). Since the recovered product DAS is a common fertiliser, ammonia stripping can also be regarded as nitrogen recovery.

2.3 Case study Braunschweig

In almost all cases of P-recovery and N-elimination and/or recovery, the system boundary ends with the production of the fertiliser. For some of the technologies implemented for P-recovery, manufacturing/operating companies state that the recovered products can be used as fertiliser, but in all cases, there is no concept for the reuse of recovered fertilisers adapted to agricultural demands.

The aim of this study is to close this gap between fertiliser production and -use and to integrate agricultural requirements and stakeholders into nutrient recovery concepts.

The study is performed for the wastewater treatment system of Braunschweig. The operators of the WWTP are currently planning to implement a MAP (magnesium-ammonium-phosphate)-precipitation and a NH_3-stripping (recovering nitrogen as ammonium sulphate, DAS) as a separate treatment for sludge liquor. Besides wastewater treatment, the use of the eliminated/recovered nutrients in agriculture is explicitly addressed, so the theoretical approach can be combined with a full-scale case study.

Moreover, treated wastewater of the Braunschweig WWTP is used for irrigation of agricultural land since more than 60 years. Besides, digested sludge is added to the irrigation water as a fertiliser. Thus, there is a long-lasting experience of the use of wastewater-related products in agriculture. The irrigation is managed by the "Abwasserverband Braunschweig" (Wastewater Board of Braunschweig), who also provided all data related to crop cultivation and fertilisation.

Due to the irrigation of digested sludge during the vegetation period, sludge dewatering and treatment of sludge liquor is only needed for slightly less than half a year, from approx. October to March. Therefore, the following study bases on a half-year operation of the recovery facilities and focuses on the options to use the recovered fertiliser in agriculture and its economic consequences. These aspects are part of a comprehensive evaluation of the nutrient recovery, including an economic feasibility study of the whole system.

3. Fertiliser production

In case of the wastewater treatment plant of Braunschweig (350.000 population equivalents), the mean daily production of process water from sludge dewatering is about 613 m³ with a mean NH_4-N concentration of 1,080 mg/L and a PO_4-P-concentration of 180 mg/L. The latter has to be regarded as rather high; this is related to the biological P-elimination without additional chemical precipitation.

There is no standard way of recovering both N and P from process water, but the technologies for the removal of the single components planned in Braunschweig – MAP-precipitation and NH_3-stripping – are quite common. Based on the literature, the removal efficiency of a MAP-precipitation can be set to 100%; the efficiency of the NH_3-stripping to 90% (ISWW 2005). Since the stripping will be implemented after the precipitation, the NH_4-N concentration in its inflow will be reduced to the amount of NH_4-N fixed in the MAP-precipitate. Table 2 gives an overview of the main parameters of nutrient recovery and the resulting fertiliser production.

Table 2: Nutrient recovery and fertiliser production, case study Braunschweig (approx. half-hear operation of MAP-precipitation and NH_3-stripping; see explanation in chapter 2.3)

Parameter	Input of recovery step (and recovery ratio)	Nutrient recovery [t/a]	Fertiliser production
NH_4-N	1,000 mg/L (90%)	96.5 t/a of N	1,110 t/a ammonium sulphate (DAS)*
PO_4-P	180 mg/L (100%)	19 t/a of P (44 t P_2O_5)	152 t/a MAP**

**40.9%-solution with a N-concentration of 8.7% **with 12.5% phosphorus*

During the half-year operation of the recovery plant, 96.5 t of Nitrogen can be revered as DAS and 19 t of P as MAP. Since fertiliser demand is only in spring/early summer (see chapter 4), the main share of the fertiliser production has to be stored.

4. The agricultural demand of fertiliser

Figure 1 gives an overview of the crops cultivated on the fields of the Wastewater Board of Braunschweig. The total cultivated area is about 2,700 hectares. The remarkable increase of corn cultivation in 2005/2006 is related to the construction of a biogas plant owned by the Wastewater Board, fed mainly with corn.

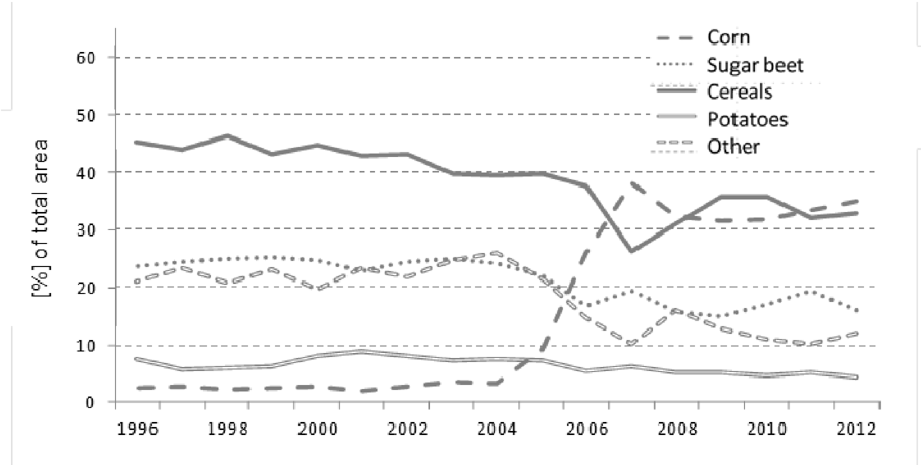


Figure 1: Percentage of area of the main crops cultivated in the area (related to the whole area of 2,700 ha)

Within this case study, the mean N- and P-demand of the four main crops (corn, wheat, sugar beet, rye) has been evaluated, using the field record system of the farmers organised in the Wastewater Board.

4.1 Phosphorus demand

Due to the irrigation of digested sludge, the additional phosphorus demand of the crops is generally very low. The only crop with a substantial demand is corn, where additional phosphorus is needed during the drilling of the seeds. Table 3 gives an overview of the summarised P-demand (as P_2O_5) of all corn fields in the Board's area (approx. 900 ha).

Table 3: Demand of phosphorus fertiliser of corn

Crop	Cultivated area	Sum of P_2O_5-demand [t/a]	Whereof DAP [t/a] (% related to sum)	Other fertiliser[t/a] (% related to sum)
Corn	ca. 900 ha	74	60 *(81%)*	14 *(19%)*

Apart from some exceptions, the whole P-demand of corn is covered by di-ammonium-phosphate (DAP).

4.2 Nitrogen demand

In contrast to phosphorus, all crops need additional nitrogen, provided by different types of fertiliser. Table 4 gives an overview of the nitrogen demand of the whole area, specified by crop and type of fertiliser.

Table 4: Demand of nitrogen fertiliser of the four main crops

Crop	Cultivated area	Total N-demand	Whereof UAN	Whereof CAN	Whereof Urea	Other fertiliser
		(all data in [t/a]; % related to the total demand of the specific crop)				
Corn	Approx. 900 ha	133	60 *(45%)*	13 *(9%)*	19 *(14%)*	41 *(31%)*
Wheat	Approx. 500 ha	85	77 *(91%)*	0	0	8 *(9%)*
Sugar beet	Approx. 450 ha	69	18 *(26%)*	16 *(23%)*	22 *(32%)*	13 *(19%)*
Rye	Approx. 250 ha	25	25 *(100%)*	0	0	0
Sum		312	180 *(58%)*	29 *(9%)*	41 *(13%)*	62 *(20%)*

UAN = Urea ammonium nitrate; CAN = Calcium ammonium nitrate

The total N-demand of the four main crops sums up to over 300 tons/year. The fertilisers used depend on the crop; for example, the N-demand of rye is completely covered by UAN, which is also the most important N-fertiliser of the whole area. In contrast, a wide variety of fertiliser is used to cover the N-demand of sugar beet, whereof only 26% are UAN.

Since UAN is the most important nitrogen fertiliser of the area, the following figure gives an overview of the times of the UAN application, classified into periods of ½ month. For all crops, there is no fertiliser application after July.

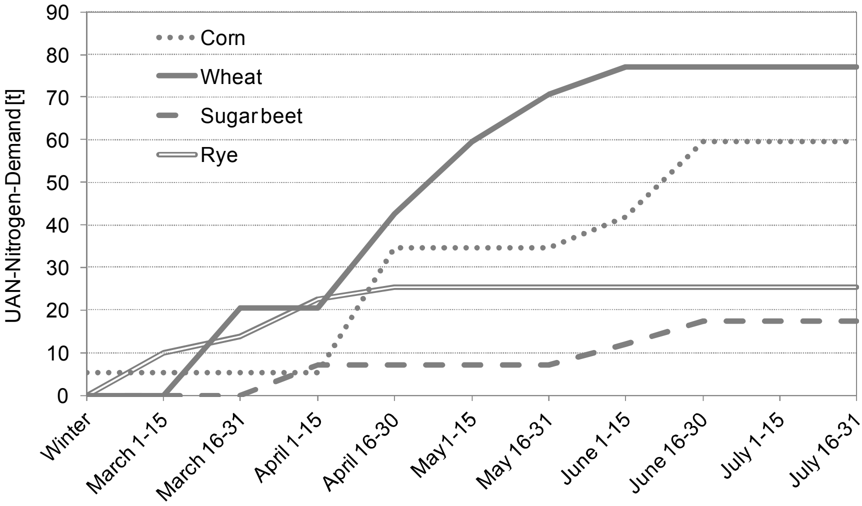


Figure 2: Summarised UAN-application/demand of the four main crops

5. Adaptation of production and demand

In this chapter, concepts for the substitution of mineral fertiliser by the recovered fertiliser will be developed.

5.1 Phosphorus

DAP is the only P-fertiliser that is currently used in substantial amounts; MAP can therefore only be used as a substitution for this fertiliser and only for corn (see table 3).

Since the half-year MAP-production of 44 t P_2O_5 is only sufficient to cover 75% of the DAP-demand, 25% of the P-demand has to be covered by mineral P-fertiliser even after the substitution. Figure 3 shows exemplarily how MAP can be used. In this case, 75% of the DAP-demand is substituted by MAP during the whole fertilisation period.

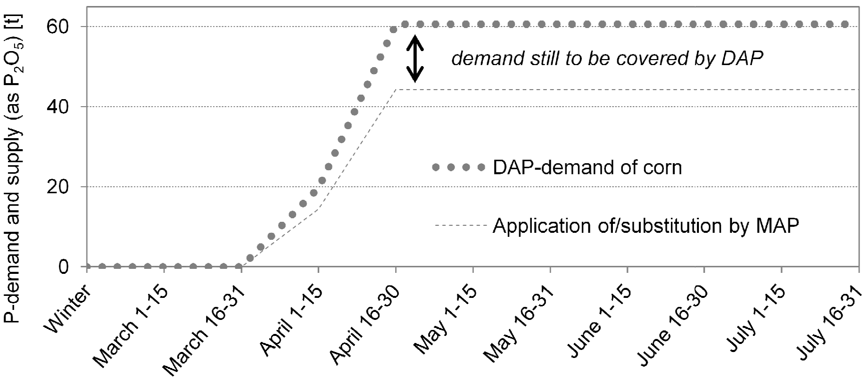


Figure 3: Substitution of 75% of the DAP-demand of corn by MAP

Commonly, the economic evaluation of MAP production considers the price/value of MAP if used in industry or calculates the theoretic value of MAP based on its single components (N, P, Mg) (Dockhorn 2009). The latter can be regarded as a benchmark to be achieved, but the value that can actually be realised depends on the intended use of MAP – e.g. a specific substitution concept –, considering the secondary effects of the substitution. In any case, the value of MAP (and all other fertilisers) depends strongly on the developments of the global fertiliser market.

Since the nutrient composition of MAP and DAP is different, their value cannot directly be compared. In a first step, the “basic” value of MAP is therefore calculated for the main nutrient which is in the focus of the substitution concept – in this case, phosphorus. Other nutrients are considered later on. Since the P-content of MAP differs from DAP (29% P_2O_5 compared to 46%), the amount of MAP needed to provide the same amount of phosphorus (=the nutrient focused on) is about 60% higher. Given a DAP-price of approximately 500 €/t in summer 2013 (VHE 2013), the basic value of MAP is calculated to 315 €/t.

Considering the other nutrients, MAP only contains 1/3 of the nitrogen of DAP. If DAP is substituted by MAP, the nitrogen application is lower and has to be compensated by other N-fertiliser. Economically, this side effect reduces the value of 1 t of MAP by 60 €/t. On the other hand, MAP contains magnesium that can substitute Mg-fertilisation. Thus, this secondary effect of the substitution leads to an economic benefit. In case of the Braunschweig system, the demand of additional Mg-fertilisation is low, so only 40%

of the Mg contained in MAP can be economically considered, corresponding to a benefit of 42 €/t MAP.

Also due to the different P-content, the application costs of MAP are higher than those of DAP. The costs have been estimated using the calculation tool of different agricultural processes provided by KTBL (2013). Table 5 gives an overview of the resulting value of MAP as a substitute for DAP.

Table 5: Value of MAP

Basic value of MAP providing the same amount of P (*VHE 2013*)	315 €/t
Additional application costs	- 6.50 €/t
Additional N-fertiliser needed*	- 60 €/t*
Benefit of Mg-application	42 €/t
Value of MAP as a substitute of DAP	**290.5 €/t**

**it should be pointed out that the nitrogen contained in MAP of course has an economic value. In this approach, the value is considered in the basic value which bases on a fertiliser that contains P and N. In contrast to this, the basic value in case of the substitution of a "P-only"-fertiliser would be lower; but then, the nitrogen contained in MAP could be (comparable to Mg) considered as a benefit. In total, it is to assume that the value of P and N contained in MAP is – independently of the specific substitution concept – more or less comparable.*

At the price level of 2013, the value of MAP if used as a substitute of DAP can be set to 290.5 €/t. The secondary effects of the substitution largely balance each other, so the value is only slightly lower than the value of MAP without considering the secondary effects.

5.2 Nitrogen

As shown in table 4, there are three main N-fertilisers that are currently used in the Board's area. Since the fertiliser produced on the WWTP (DAS) only contains NH_4-N, the substitution concept should focus on a fertiliser with comparable properties, i.e. UAN. In this case, the application method has not to be changed, because both UAN and DAS are liquid (in contrast to CAN and Urea that are also used in the area).

The half-year DAS-production of 96.5 t nitrogen theoretically would be sufficient e.g. to cover the whole UAN-demand of wheat and sugar beet (see table 4). Since the specific properties of DAS are different to those of UAN, it seems not reasonable to substitute the UAN-demand of one crop completely. To avoid possible problems related to the different properties of DAS (especially the high sulphur content), the following concept focuses on the substitution of one UAN-application by DAS for all crops (table 6).

Table 6: Substitution of UAN by DAS

Crop	Cultivated area	Mean quantity of *one* UAN-application	Total quantity of DAS needed if *one* application of UAN is substituted
Corn	Approx. 900 ha	57 kg/ha	51.5 t/a
Wheat	Approx. 500 ha	43 kg/ha	21.5 t/a
Sugar beet	Approx. 450 ha	15 kg/ha	7 t/a
Rye	Approx. 250 ha	49 kg/ha N	12.5 t/a
Sum			**92.5 t/a**

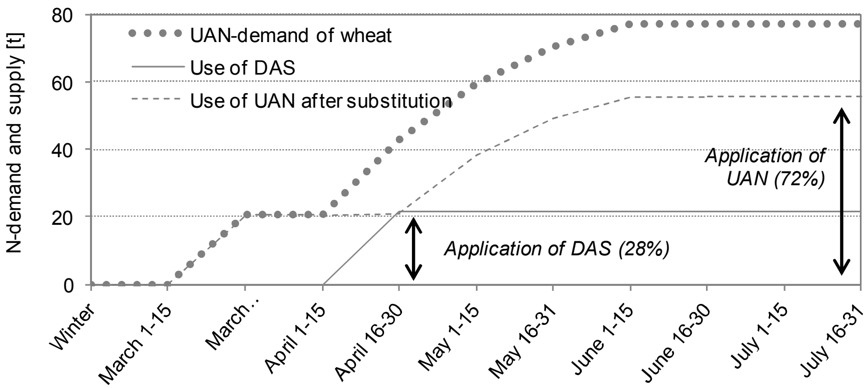


Figure 3: Substitution of one UAN-application by DAS in case of wheat

Within this substitution concept, 92.5 t of UAN is substituted by DAS. Figure 3 shows exemplarily how DAS can be used for the fertilisation of wheat; in this case, the UAN-application in April is substituted by DAS. Since the total UAN-demand of wheat is very high (see table 4), the relation of DAS compared to the total UAN-demand is only 28%.

As for MAP, the economic evaluation of DAS usually considers the price/value of DAS if used in industry or calculates the theoretic benchmark. Again, the value that can actually be realised depends on the specific substitution concept, considering the secondary effects of the substitution.

Since the mass-related N-content of DAS differs from UAN (8.6% N compared to 30%), the value of 1 ton of DAS can be set to ~30% of the value of 1 t of UAN. Given a UAN-price of approximately 270 €/t in summer 2013 (VHE 2013), the price of DAS is calculated to 77 €/t. Also due to the different N-content, the amount of DAS needed is about 3.5 times higher than the amount of UAN. This leads to notably higher application costs that have also been calculated by the KTBL-tool (KTBL 2013). Moreover, the acidity of DAS is higher than the acidity of UAN and has to be buffered by lime. Economically, this secondary effect reduces the value of DAS.

Comparably to the Mg-application in case of the MAP/DAP-substitution, the sulphur content of DAS can theoretically be regarded as a benefit, but since the sulphur demand in the area is low, it cannot be considered economically. Table 5 gives an overview of the resulting value of DAS as a substitute for UAN.

Table 7: Value of DAS

Value of DAS related to the N-content (*VHE 2013)*	77 €/t
Additional application costs	- 16.40 €/t
Additional demand of lime	- 12 €/t
Value of DAS as a substitute of UAN	**48.6 €**

At the price level of 2013, the value of DAS if used as a substitute of UAN can be set to 48.6 €/t. In this case, the secondary effects of the substitution have a great influence on the value of the substitute.

5.3 Price of the fertiliser

If MAP and DAS are sold for their specific substitution value of 290 €/t and 48.6 €/t, there is no economic benefit of the substitution on the *agricultural* side. On the other hand, the agricultural use would lead to no benefit for the *producers* if the prices are lower than the achievable prices if the recovered products are sold to industry. Table 8 gives an overview on the maximal and minimal prices of the fertiliser.

Table 8: Minimal and maximal price of the recovered fertilisers

	MAP	**DAS**
Maximum price = value as a substitute for DAP and UAN, respectively (see tables 5 and 7)	290 €/t	48.60 €/t
Minimal price = value if sold to industry (*UBA 2007, PFI 2012*)	60-100 €/t	25 €/t

Any price between these benchmarks will lead to a win-win-situation for both stakeholders that can be regarded as a crucial aspect for the implementation and the acceptance of a reuse system. Depending on the specific use/substitution concept, the maximum values might be higher or lower, thus extending or narrowing the margin for a win-win situation.

6. Conclusion

The previous study focused on the integration of the agricultural stakeholders into nutrient recovery concepts. This is the basis to set up substitution concepts and to determine the “real” value of a fertiliser that is used as a substitute. In case of the system of Braunschweig, MAP and DAS shall be used as a substitute for DAP and UAN, respectively. The calculated values, considering all secondary effects of the substitution, are still notably higher than the reference values of an external (industrial) use. Thus, a win-win-situation for both stakeholders can be created, which will be a crucial aspect for the acceptance of the agricultural reuse.

Compared to the total costs of the nutrient recovery, the revenue generated by the agricultural reuse is relatively low. But given the fact that reuse systems are under certain circumstances considered to be close to economic feasibility (Sartorius 2011) – a conclusion that also can be drawn specifically for the system of Braunschweig –, even small differences of the benefits can be the decisive factor whether implementing a system or not.

Thus, the integration of the agricultural side, the development of substitution concepts and the agreement of a win-win-price is also a crucial aspect from the economic point of view. Additionally, the agricultural reuse leads to non-economic benefits such as the protection of limited resources.

References

Dockhorn, T. (2009): About the economy of phosphorus recovery. In: Ken Ashley et al (Eds.): International conference on nutrient recovery from wastewater streams, IWA Publishing, London, pp. 145-158

Egle, L., Reichel. M. (2012): Stand und Trends bei der Nährstoffrückgewinnung auf Kläranlagen. ÖWAV-Seminar "Standortbestimmung in der Wassergütewirtschaft", Wien, 23./29.02.2012

Elsner, H. (2008): Stand der Phosphat-Reserven weltweit. Beitrag zu den Braunschweiger Nährstofftagen 2008 „Ressourcen schonender Einsatz von Phosphor in der Landwirtschaft“, JKI-Institut Braunschweig, 10.-11.11.2008

Herrmann, L. (2009): Rückgewinnung von Phosphor aus der Abwasserreinigung – Eine Bestandsaufnahme. Umwelt-Wissen Nr. 0929, Bundesamt für Umwelt Bern, 196 pp.

ISWW (2005): Untersuchung der Behandlungsmöglichkeiten von Zentratwasser aus der Schlammentwässerung auf dem Gelände des Klärwerks Steinhof. Unveröffentlichte Studie des ISWW Braunschweig, Mai 2005

Jardin, N., Arnold, E., Beier, M., Grömping, M., Kolisch, G., Kühn, V., Meyer, S., Rolfs, T., Schmidt, F., Wett, B., Otte-Witte, R. (2005): Rückbelastung aus der Schlammbehandlung – Verfahren zur Schlammwasserbehandlung. 4. DWA-Klärschlammtage, Würzburg, April 2005, 20 pp.

KTBL (2013): Feldarbeitsrechner. Kostenpflichtiger Zugang unter http://www.ktbl.de/index.php?id=806

PFI (2012): Mündliche Auskunft des Planungsbüros PFI

Pinnekamp, J., Gethke, K., Montag, D. (2005): Stand der Phosphorrückgewinnung. In: 38. Essener Tagung für Wasser- und Abfallwirtschaft; Schriftenreihe Gewässerschutz-Wasser-Abwasser Nr. 198, Aachen 2005, pp. 73/1-73/8

Sartorius, C. (2011): Technologievorausschau und Zukunftschancen durch die Entwicklung von Phosphorrecyclingtechnologien in Deutschland. In: Pinnekamp (Hrsg.): Förderinitiative „Kreislaufwirtschaft für Pflanzennährstoffe…“; Gewässerschutz-Wasser-Abwasser Nr. 228, Aachen 2011, pp. 12/1-12/20

UBA (Hrsg., 2007): Rückgewinnung eines schadstofffreien, mineralischen Kombinationsdüngers „Magnesiumammoniumphosphat – MAP“ aus Abwasser und Klärschlamm. Bericht im Auftrag des Umweltbundesamtes von Pinnekamp et al; 2. Auflage, Umweltbundesamt, Dessau-Roßlau

VHE (2013): Wert des Kompostes/Reinnährstoffpreise. Ständig aktualisierte Informationen; verfügbar unter http://www.vhe.de/aktuelles/kompostwert-der-kompostpreis/

Author

Dipl.-Geoökol. Daniel Klein

Technische Universität Braunschweig, Institute of Sanitary and Environmental Engineering

Pockelsstrasse 2a, 38106 Braunschweig, Germany

d.klein@tu-bs.de

Veröffentlichungen

des Instituts für Stadtbauwesen, Abt. Siedlungswasserwirtschaft, TU Braunschweig

Heft 1*	R. Kayser Ermittlung der Sauerstoffzufuhr von Abwasserbelüftern unter Betriebsbedingungen (1967)	
Heft 2	E. Zingler Die Filtration von Abwasserschlämmen – Grundlagen und Modellversuche (1969)	13,- Euro
Heft 6*	E. Zingler Die Filtration von Abwasserschlämmen II – Die Übertragbarkeit von Laboratoriumsergebnissen auf den technischen Betrieb (1970)	
Heft 15	J. Knoch Untersuchung und biologische Reinigung von Sickerwasser aus Mülldeponien (1974)	13,- Euro
Heft 19*	FESTSCHRIFT FÜR HEINRICH HABEKOST Teil 2: Siedlungswasserwirtschaft (1976)	
Heft 21*	R. Stegmann Auswertung und Prognose von Gewässergütedaten, dargestellt am Beispiel von Meßwerten der Oker und ihrer Nebenflüsse (1976)	13,- Euro
Heft 23	K. Korn Metallgehalte im Sickerwasser von Mülldeponien Ergebnisse von zweijährigen Untersuchungen an 14 Deponien (1977)	13,- Euro
Heft 25*	D. Bahrs Konditionieren von Abwasserschlämmen durch Gefrieren (1978)	13,- Euro
Heft 26*	H.-J. Ehrig Beitrag zum quantitativen und qualitativen Wasserhaushalt von Mülldeponien (1978) zweite erweiterte Auflage (1980)	
Heft 27*	R. Stegmann Reinigung und Verregnen von Müllsickerwasser unter Betriebsbedingungen - dargestellt am Beispiel der Deponie Venneberg/Lingen (1979)	
Heft 28*	W. Walther Beitrag zur Gewässerbelastung durch rein ackerbaulich genutzte Gebiete mit Lössböden (1979)	
Heft 29*	ASPEKTE DES STADTBAUWESENS zum 70. Geburtstag von Heinrich Habekost Teil B: Siedlungswasserwirtschaft	
Heft 33	Gas- und Wasserhaushalt von Mülldeponien INTERNATIONALE FACHTAGUNG (29.09.-01.10.1982) in Braunschweig	20,- Euro
Heft 34*	Anthropogene Einflüsse auf die Grundwasserbeschaffenheit in Niedersachsen, Fallstudien 1982 TAGUNG (14.-15. Oktober 1982) in Braunschweig	
Heft 35*	G. Ermel Stickstoffentfernung in einstufigen Belebungsanlagen – Steuerung der Denitrifikation (1983)	
Heft 38	Ablagerung umweltbelastender Stoffe Fachseminar 06.-07. Februar 1985 in Braunschweig	20,- Euro
Heft 39*	Sickerwasser aus Mülldeponien – Einflüsse und Behandlung – Fachtagung 21.-22. März 1985 in Braunschweig	
Heft 40	W. Walther, B. Scheffer und B. Teichgräber Ergebnisse langjähriger Lysimeter-, Drän- und Saugkerzen-Versuche zur Stickstoffauswaschung bei landbaulich genutzten Böden und Bedeutung für die Belastung des Grundwassers (1985)	15,- Euro
Heft 41	H.-J. Ehrig Weitergehende Reinigung von Sickerwässern aus Abfalldeponien (1987)	20,- Euro
Heft 42*	Biologische Stickstoff- und Phosphorelimination in Abwasserreinigungsanlagen Weiterbildungsseminar 26.-27. März 1987 in Braunschweig	20,- Euro

Nach Abtrennung der Abt. Siedlungswasserwirtschaft vom Institut für Stadtbauwesen wird die Reihe ab Heft 43 weitergeführt als:

Veröffentlichung des Instituts für Siedlungswasserwirtschaft der TU Braunschweig

Heft 43	Rashed M. Y. Al-Sa'ed Untersuchungen zur Nitrifikation von Abwässern mit hohen Ammoniumgehalten in Belebungsanlagen INVESTIGATIONS ON NITRIFICATION PROCESS OF AMMONIUM-RICH WASTEWATER IN SINGLE STAGE ACTIVATED SLUDGE SYSTEMS Braunschweig (1987)	20,- Euro
Heft 44*	Artur Mennerich Beitrag zur anaerob-aeroben Behandlung von Sickerwässern aus Hausmülldeponien (1988)	
Heft 45*	Burkhard Teichgräber Zur Nitrifikation von Abwässern mit geringer Säurekapazität (1988)	
Heft 46	Reiner Boll Zur erhöhten biologischen Phosphorentfernung mit dem Belebungsverfahren (1988)	20,- Euro
Heft 47	R. Kayser, Ch. Wolffson (Herausgeber) Kläranlagen zur Stickstoff- und Phosphorelimination Weiterbildungsseminar 16.-17. März 1989	20,- Euro
Heft 48*	W. Walther (Herausgeber) Grundwasserbeschaffenheit in Niedersachsen – Diffuser Nitrateintrag, Fallstudien Weiterbildungsseminar, 21.-22. Februar 1990	
Heft 49	Henning Albers Zur biologischen Reinigung von Sickerwasser aus Sonderabfalldeponien (1991)	20,- Euro
Heft 50	Rolf Kayser (Herausgeber) Vergleich verschiedener Bemessungsansätze zur Stickstoffelimination und Garantien fürBelüftungseinrichtungen Fachtagung 09.-10. September 1991	20,- Euro
Heft 50 E	Rolf Kayser (Editor) Workshop Nitrogen Removal and Aeration Guarantees, September 9 and 10, 1991 (Englische Originalbeiträge)	15,- Euro
Heft 51	Heribert Dernbach Nutzung von Deponiegas mit hohem HKW-Gehalt und Möglichkeiten der Behandlung (1991)	20,- Euro
Heft 52	Christian Wolffson Denitrifikation von speziellen Abwässern mit externen Kohlenstoffquellen (1992)	20,- Euro
Heft 53	Michael Werner Deponiegas zur Denitrifikation von Sickerwasser aus Mülldeponien (1993)	20,- Euro
Heft 54	Klaus Kruse Langfristiges Emissionsverhalten von Siedlungsabfalldeponien (1994)	20,- Euro
Heft 55	Joseph Hölscher Stickstoffbilanz für ein durch Kiesgewinnung gestörtes Grundwasser in einem Wassereinzugsgebiet (1994)	20,- Euro
Heft 56	Gösta Ladiges Expertensysteme für Kläranlagen unter besonderer Berücksichtigung der Stickstoffelimination in einstufigen Belebungsanlagen (1994)	20,- Euro
Heft 57	Thomas Teichfischer Der Einfluß schwankender Abwasserzusammensetzungen auf die vermehrte biologische Phosphatelimination und Möglichkeiten zur Prozessstabilisierung (1994)	20,- Euro
Heft 58	Hartmut Wicht N_2O-Emissionen durch den Betrieb biologischer Kläranlagen (1996)	20,- Euro
Heft 59	Thomas Nellenschulte Modell zur Charakterisierung des Entwässerungsergebnisses von Klärschlämmen (1996)	20,- Euro

Heft 60	Bernd Zacharias Biologische Stickstoffelimination hemmstoffbelasteter Abwässer am Beispiel eines Eisenhüttenwerks (1996)	20,- Euro
Heft 61	J. Müller, N. Dichtl, J. Schwedes (Herausgeber) Klärschlammdesintegration – Forschung und Anwendung Fachtagung 10./11. März 1998	20,- Euro
Heft 62	Liendel Chang Auslegung von einstufigen Belebungsanlagen zur Stickstoffelimination bei Sickerwässern aus Siedlungsabfalldeponien (1998)	20,- Euro
Heft 63	Martin Steensen Chemische Oxidation und biologische Nachreinigung zur weitergehenden Sickerwasserbehandlung (1998)	20,- Euro
Heft 64	Thomas Dockhorn CSB-Elimination in Abhängigkeit vom Typ des Belebungsbeckens (1999)	20,- Euro
Heft 65	Franziska Gromadecki Anwendungsorientierte Betriebsoptimierung von Sickerwasserreinigungs-anlagen (2000)	20,- Euro
Heft 66	Julia Kopp Wasseranteile in Klärschlammsuspensionen – Messmethode und Praxis-relevanz – (2001)	20,- Euro
Heft 67	Lars Keudel Bestimmung des Absetzverhaltens von belebtem Schlamm zur Bemessung von Kläranlagen nach dem Sequencing Batch Reactor (SBR)-Verfahren (2002)	20,- Euro
Heft 68	Markus Engelhart Anaerober Abbau mechanisch desintegrierten Überschussschlammes (2002)	20,- Euro
Heft 69	Rolf Kloss Vergleich von Verfahren und Reaktoren zur anaeroben Behandlung von Substraten mit hohem Anteil an groben suspendierten Feststoffen (2002)	20,- Euro
Heft 70	Anke Winter Desintegrationsverfahren zur Intensivierung der Schlammfaulung – Großtechnische Vergleiche – (2003)	20,- Euro
Heft 71	Matthias Wittenberg Stoffstromanalyse und Bewertung von Umweltschutzmaßnahmen am Beispiel der Abwasserwirtschaft eines Automobilwerks (2003)	20,- Euro
Heft 72	Uwe Moshage Rheologie kommunaler Klärschlämme - Messmethoden und Praxisrelevanz- (2004)	20,- Euro
Heft 73	Rayko Jordan Vegetative Behandlung anaerob stabilisierter Klärschlämme (2005)	20,- Euro
Heft 74	Thomas Dockhorn Stoffstrommanagement und Resourcenökonomie in der kommunalen Abwasserwirtschaft (2007)	20,- Euro
Heft 75	Samir Naser Hag Irahim Structure, Function and Formation of Anaerobic Granular Sludge (2008)	20,- Euro
Heft 76	Stefanie Wolter Untersuchungen zur Substratabhängigkeit des heterotrophen Ertragskoeffizienten (2009)	20,- Euro
Heft 77	2. Internationales Symposium Abwasserrecycling 04. - 06.11.2009 "Abwasserrecycling – Chancen und Risiken" Tagungsband	20,- Euro
Heft 78	Kai Klinksieg Charakterisierung des Absetzverhaltens von kommunalen Klärschlämmen mit Hilfe rheologischer Messungen (2010)	20,- Euro
Heft 79	Lars Günther Großtechnische Nährstoffrückgewinnung und Schadstoffausschleusung aus kommunalen Klärschlämmen (2011)	20,- Euro

Heft 80	Mohamed Rabie Mohamed Ghazy Sustainable Sewage Sludge Management in Egypt Based on Life Cycle Assessment (2011)	20,- Euro
Heft 81	3. Internationales Symposium Re-Water Braunschweig 21. - 22.11.2011 "Implementierung und Realisierung" Tagungsband	20,- Euro
Heft 82	Katrin Bauerfeld Einfluss klimatischer Randbedingungen auf die Klärschlammentwässerung (2012)	20,- Euro
Heft 83	Timur Esemen Untersuchungen zur technischen und wirtschaftlichen Optimierung der Nährstoffrückgewinnung aus Klärschlamm (2012)	20,-Euro
Heft 84	4. International Symposium Re-Water Braunschweig 06.-07.11.2013 "Quality, Reuse, Global aspects" Conference Proceedings	20,- Euro

*vergriffen

Veröffentlichungen des Institutes für Siedlungswasserwirtschaft der Technischen Universität Braunschweig

Heft 84

Herausgeber:
Gesellschaft zur Förderung des Institutes für Siedlungswasserwirtschaft an der Technischen Universität Braunschweig e.V.

Braunschweig 2013 ISSN 0934-9731 DOI 10.24355/dbbs.084-202103230745-0